ULTRASONIC PHYSICS

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ULTRASONIC PHYSICS

by

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NON SOLUS

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PREFACE

To write a book on a subject so much experimented upon as ultrasonics requires some justification, especially as there are several excellent books already published on the subject. My excuse must be that the emphasis in these books is on applications particularly in industry, whereas the main theme of mine is the ultrasonic interferometer as precision tool in the physics laboratory. More and more of late years has the attitude of physicists and physical chemists to this subject turned from "what can we find with this new tool" to "what accuracy are we justified in expecting of it and is it as precise as, for example, the grating spectrometer in optics?"

If in this discussion I have devoted too much space to the work in which I have been directly concerned or seen in operation in friends' laboratories, my excuse must be the author's usual one that he writes best of what he knows best. I have however, attempted to deal honestly with all published work and give extensive references at the end of each chapter. Those who want more or wish to add to them may find bibliographies in the *Journal of the Acoustical*

Society (abbreviated to *J.A.S.A.* in my references), and in the *Progress Reports of the Physical Society* (London).

The tables of propagation constants which I give at the ends of Chapters IV and V embrace most of the common fluids but are much condensed, serving to indicate the range of frequency, temperature, *etc.* which have been covered in experiments up to the present time. I assume the reader will seek details in the original papers to which he is referred in the succeeding bibliographies.

I record with pleasure the collaboration of former research students and colleagues at Newcastle, over the past twenty years, and I am particularly grateful to three present colleagues Drs. J. F. W. BELL, L. E. LAWLEY, and H. R. THIRSK and to Dr. A. SCHALLAMACH of Welwyn who have made helpful criticism of my manuscript or submitted pages for it.

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E. G. RICHARDSON

Newcastle-on-Tyne,
October, 1951

CONTENTS

Preface v

I. Sources of Ultrasonics 1

1. Piezo-electric Source 3
2. Cutting the Oscillator 5
3. Mounting of Quartz 11
4. Circuits to Maintain Piezo-electric Oscillators 14
5. Impedance of Crystal Oscillator 19
6. Magneto-strictive Oscillator 23
7. Ferro-electric Crystals 26
8. Electro- or Magneto-strictive Transducers 27

References 30

II. Methods of Detection and Properties of Ultrasonic Radiation 32

1. Smoke Method 33
2. Behaviour of a Large Obstacle in the Field 34
3. Radiometers 37
4. Electrical Detectors 40
5. Optical Methods 43
6. Microphones 45
7. Radiation from a Disc 46
8. Reaction on Source 54
9. Change of Wave-Form 56

10. "Streaming" from an Acoustic Source 57
11. Cavitation 59
12. Scattering of Ultrasonics by Obstacles 61
References 66

III. MEASUREMENTS OF PROPAGATION CONSTANTS 68

1. The Pierce Interferometer 68
2. The Fixed-Path Interferometer 71
3. The Variable-Path Interferometer 73
4. Thermal Absorption 78
5. Satellites: Effects of Radial Waves 79
6. Viscous Damping in Narrow Tubes 85
7. Pulse Methods for Propagation Constants 87
8. Velocity in Liquids by Optical Methods 90
9. Ultrasonic Wave-Train as Optical Grating 93
References. 100

IV. PROPAGATION IN GASES 102

1. Low Frequency Measurements 102
2. Ultrasonic Propagation in Pure Gases. 106
3. Propagation in Vapours 116
4. Propagation in Moist Air 120
5. Propagation in Other Mixtures of Gases. 125
6. Effects of Pressure and Temperature 128
7. Propagation at High Temperatures and Pressures. . . . 137
8. Effects at Low Temperature 143
9. Propagation in Gases contained in Capillary Tubes . . . 147
References. 155

V. PROPAGATION IN LIQUIDS 158

1. Continuous Wave Methods in Liquids 159
2. Pulse Methods for Absorption 168
3. Reverberation Methods for Absorption 170

4. Absence of Dispersion of Velocity in Liquids. . . . 172
5. Attenuation in Liquids 176
6. Results for V and α in Liquid Mixtures 178
7. Influence of Pressure and Temperature 181
8. Effect of Varying Temperature. 183
9. Propagation in Condensed Gases 186
10. Measurement of Ionic Solvation in Electrolytes . . . 187
11. Ionic Effects in Practice 190
12. Elastic Liquids under Shear and Compressional Vibration 192
13. Velocity in Liquid Helium 201
References 209

VI. PROPAGATION IN SOLIDS 213

1. Plates 213
2. Propagation in Rods 214
3. Propagation in Rubber-like Materials 224
4. Propagation in High Polymers and Fibres 227
5. Ultrasonic Lenses 229
References 230

VII. THEORIES OF ANOMALOUS PROPAGATION 232

1. Relaxation Theory 232
2. Application of Theory to Gases 238
3. Scattering and Diffusion Theories. 242
4. Application to Liquids 244
5. Absorption in Solids 247
6. Propagation in Liquid He II 248
References 250

VIII. ULTRASONICS IN DISPERSE SYSTEMS 252

1. Propagation in Aerosols 252
2. Acoustic Birefringence 260
3. Vibrating Bubbles and Drops 263

4. Dispersion and Coagulation of Particulate Matter . . 267
5. Grain Refining and Ultrasonic Scattering in Melts . . 270
6. Break-up of Jets. Formation of Emulsions 274
References 277

INDEX 279

CHAPTER I

SOURCES OF ULTRASONICS

Ultrasonics, in the sense of artificially produced compressional waves at frequencies too high to affect the human ear — in effect, above 20,000 c/sec — may be said to have been known since 1883 when GALTON adapted the edge tone generator to determine the upper limit of pitch sensation in human beings. When, in fact, a jet of air debouches from a narrow slit to fall upon the sharp edge of an object which faces the slit, the jet is set in pendulation and in so doing may set up a musical tone in the surrounding medium. The frequency f of this edge tone is related to the velocity U of the jet and the distance l separating slit and edge by a relation of the type U/lf = constant.

GALTON raised the velocity of efflux (by increasing the pressure in the wind chest) and reduced the separation of slit from edge until the frequency transcended the audible pitch range of his human subjects. In such an apparatus, the energy in the jet rises with the efflux velocity and in turn raises the intensity of the sound, though the latter is not large in absolute value as the conversion of energy is inefficient.

HARTMANN[1] has developed the ultrasonic jet source a step further by raising the velocity of the jet until it exceeds the velocity of sound in the air which is used in the jet. The jet of compressed air emerges from a hole to impinge on a coaxal ring-shaped edge which may be the mouth of a small bottle-resonator. Shock waves originate in the gas as it emerges into the atmosphere and are reflected from the confines of the jet in criss-cross fashion, as can be seen from a shadow photograph. If the annular edge is located in one of these circular zones of reflection as shown in Fig. 1 a powerful oscillation of the air is set up at a frequency determined by the wave-length between these zones and the velocity of the jet, consequently the pitch lies usually above the sonic range.

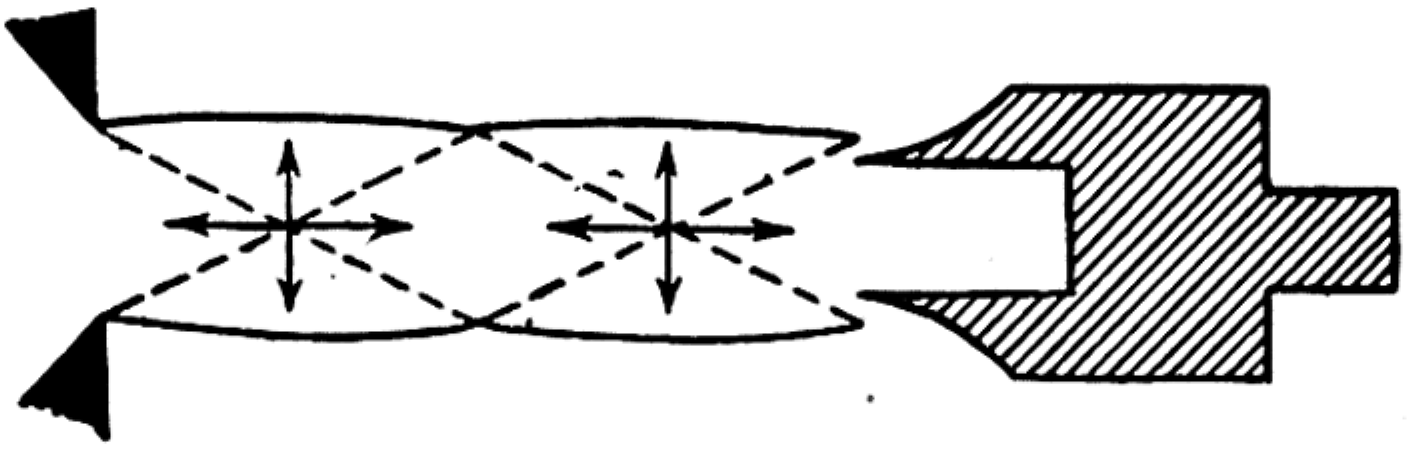

Fig. 1. Hartmann Generator

Another possible source was found in the singing arc of DUDDELL[2] (1900). In this device a direct current arc has superposed on it the oscillations in a resonant circuit consisting of an inductance L and capacitance C in parallel. The period of oscillation is given then by $2\pi\sqrt{LC}$ so that, by making L and C small enough, ultrasonic waves can be propagated into the surrounding air.

Though a considerable amount of ultrasonic energy is

References pp. 30–31

attainable from such sources, particularly from the HARTMANN generator, the vagaries of their output — both as to amplitude and frequency — and their impure quality make them unsuitable for precise measurements such as those we are going to discuss in this book. Such only became possible when some source less highly damped and so with stronger resonant characteristics had been discovered. Such sources are small solid oscillators — small, because of the requirement of short wave-length — employing either the piezo-electric or the magneto-strictive effect. Since books exist which are devoted to a discussion of the origin and practice of these two effects, particularly of the former, we shall content ourselves with a treatment of those aspects which are involved in the construction and use of sources suitable for setting up ultrasonic radiations, and refer the reader to such books if he requires more information on the fundamental aspects of piezo-electricity or magnetostriction.

1. Piezo-electric Source

Following some early inconclusive experiments relating to the production of electric charges on substances when compressed, the brothers P. and P. J. CURIE [3] in 1880 established that crystals which lack a centre of symmetry when compressed along certain axes develop positive and negative charges of magnitude proportional to the applied pressure. Later they discovered the converse effect, *viz.*, a change in the dimensions of the crystal when a potential difference is applied. The name by which this phenomenon is generally known was given to it by HANKEL, though — in view of more recent knowledge — some prefer the generic term "electro-strictive".

LANGEVIN [4] had the idea in 1917 of exciting a quartz crystal into rhythmic oscillation at one of its natural frequencies by setting it in resonance with a tuned circuit such as DUDDELL had applied to his arc. It is perhaps needless to say that this development would scarcely have been possible before the invention of the thermionic valve.

Beside quartz, a number of other piezo-electric crystals have been used as oscillators, of which the chief are: tourmaline, tartaric acid, Rochelle salt, ammonium dihydrogen phosphate (ADP) [5], and barium titanate [6]. Of these, Rochelle salt has the highest Curie constant — ratio of mechanical movement to applied voltage — but it and the first named crystals are more susceptible to fracture than quartz and are hygroscopic.

All these crystals lack a centre of symmetry and are characterised by three axes and it is at the ends of two of these axes that the charges arise when the crystal is stressed. One of these axes, referred to as *Z* axis, is the optical axis, that along which the crystal is birefringent. It can be located by passing polarised light through the crystal and finding a direction such that no variation in transmitted light occurs as the crystal is rotated about this axis. (Incidentally, a crystal which during growth has "twinned" will exhibit such variations no matter what axis is chosen for the direction of transmittion; but optical twins are rejected for our purpose). To detect the *X* and *Y* axes which are perpendicular to the *Z* axis, facets on the crystal are etched in hydrofluoric acid, and light sent up through the crystal from below to be refracted by an etched facet on emergence. If the light comes along the *Z* axis then, after refraction and emergence, the light is seen to be concentrated into three characteristic spots at the vertices of an equilateral triangle. The positions of these spots determine the location of the *X* and *Y* axes. They may also be determined from the reflection pattern of an X-ray beam directed on to one of the faces.

2. Cutting the Oscillator

The next step is to cut the quartz oscillator from the crystal. Fig. 2 shows how the commonest cuts (slabs or discs) are orientated with respect to the axes. Slabs in which the greatest dimension is along the *Y* axis and the least — the "thickness" — along the *X* axis are used as sources of ultrasonic energy from 20 to 150 kilocycles/sec, while discs, also with thickness along the *X* axis, serve up to about 20 megacycles/sec. In both cases, the potential is applied across the thickness and motion takes place along the *X* and *Y* axes.

The source is usually excited at resonance by applying an alternating potential of frequency (for the fundamental mode) $f = V/2l$, V being the velocity of sound in the material and l the characteristic length, usually the longest dimension (Y) of a slab, or the thickness (X) of a disc. Beside the fundamental, the odd harmonic overtones can be produced even up to the fiftieth, but with diminishing efficiency, making them less suitable for ultrasonic experiments than the fundamental.

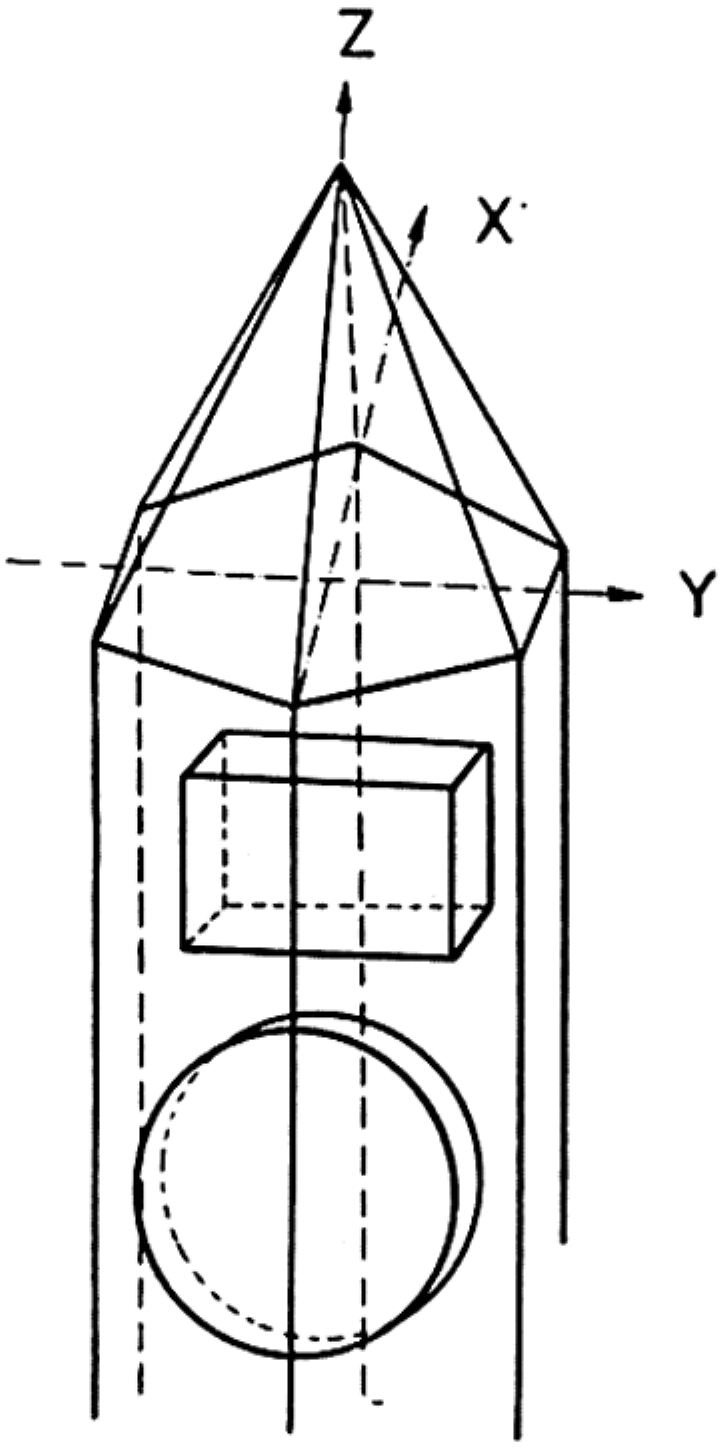

Fig. 2. X "cuts" from Quartz; Slab and Disc

The cutting is done by a revolving copper wheel dipping into wet carborundum or a diamond-studded wheel cooled by oil, or even by a thin carborundum wheel. It is possible to cut discs down to 0.2 mm thickness. Such have a fundamental frequency of 15 Mc/sec, but harmonics up to 200 Mc/sec are possible. The larger the diameter which can be given to the disc the better for ultrasonic purposes — anything from 2 to 5 cm is common. The faces are then etched and metallic coatings to form the electrodes, above and below, cemented or sputtered on to the surfaces. The metals so used are silver, gold or aluminium.

It may be necessary to reject a generator after test for one or other of the following defects; (1) one of the excitable "length" harmonics lies too close to one of the "thickness" modes, in which case one will "pull" the other and the quartz will jump from one frequency to the other. It is possible also that such coupling will occur with one of the flexural or torsional modes (*vide infra*); (2) the thickness mode presents an uneven amplitude over the vibrating surface as revealed by examination in an optical interferometer, though a certain variation in amplitude over the radiating face is permissible without causing similar variations in the medium into which it radiates; (3) there may be a tendency to set up (flexural) vibrations in the length mode, which vibrations, audible as a ringing noise, overlay the longitudinal vibrations and detract from the amount of energy passing into these desired modes of vibration. Other audible tones may be caused by "beats" between the nearby frequencies, already noted.

Several methods of examining the pattern of oscillation of the quartz are available. The oldest is that by which CHLADNI examined the modes of vibration of quartz plates, *i.e.*, by strewing sand or other powder over the surface and observing where it collects into the nodal lines.

The other two are optical methods. DYE [7] passed a beam of light through a quartz disc, letting it form one plate of an optical interferometer. When the disc is still an interference pattern of dark lines is seen in the beam several times reflected between the quartz and the other (glass) plate of the interferometer.

When the crystal is set in vibration, these broaden out or — under stroboscopic illumination — can be seen to be moving to and fro with the frequency of the crystal's vibrations. In a good generator the broadening of the lines will be fairly uniform over the surface.

This method demonstrates the surface amplitude of the quartz; that of TAWIL [8] concerns the interior motion. A beam of plane polarised light is passed through the experimental disc along its thickness — the electrodes being pierced for this purpose. It is "crossed" with an identical but stationary disc, and the pair set between two Nicol prisms so that, with both crystals quiescent, no light passes the system. If now one quartz is set in oscillation in a direction normal to the path of light, optical birefringence ensues at the nodes of the strained crystal. This results in a transmission of light at the nodes during part of the period of vibration, whereas the extinction persists in the antinodes. The nodal patterns may be photographed either in steady or stroboscopic illumination and compared with a surface study of the quartz, made by powder or interferometer photography, as described above.

Some of the non-uniformity in amplitude over the surface of the cut crystal is due to the direction of oscillation not coinciding with the axis of the disc or slab. STRAUBEL [9] noted that the two axes (*X* axis and axis of oscillation) often lay at 20° to each other, a fact that was confirmed when he observed that the nodal plane which bisects a slab when it is vibrating in its fundamental mode is likewise inclined to the *X* axis of the crystal, *i.e.*, to the vertical as the slab lies on its electrode. He therefore suggested that the cut should be made at 70° to the *Z* axis instead of at the more usual 90° so as to make the axis of the slab or disc conform to the preferred direction of vibration, which is, in fact, the direction for which the elastic modulus is a minimum. While STRAUBEL crystals have certain advantages, such as the acceptance of more power without fracture, it is doubtful whether they produce greater uniformity of amplitude in the surrounding medium than the normal 90° cut.

Other shapes beside the two already mentioned have been cut for special purposes. In particular, the plano-concave lens (GRÜTZMACHER [10]) and other forms of curved disc (LABAW [11]), the ring (CEROVSKA [11]) possess the property of an enhanced vibration or focussing effect at the centre of curvature which is, of course, outside the material and can be the site of an experiment requiring concentrated intensity. Otherwise, and for most of the work with which we are concerned in this volume, plane waves are preferable.

To maintain torsional modes of vibration, there are two possibilities. A quartz slab may be cut in the way described, the electrodes applied and immediately slit longitudinally. One lower half and the opposite upper half are joined to form one lead, the other pair of opposite segments to the other lead. So the potential gradient is directed up one side and down the other causing the slab to twist about a median axis. In Mason's[12] form of torsional generator a rod is cut along the axis and provided with four longitudinal electrodes connected alternately in pairs (Fig. 3c) (like the quadrants of an electrometer) or the rod is bored through to make a hollow cylinder and the electrodes cemented, one internally and one externally. Latterly, hollow cylinders of barium titanate have been manufactured for this purpose.

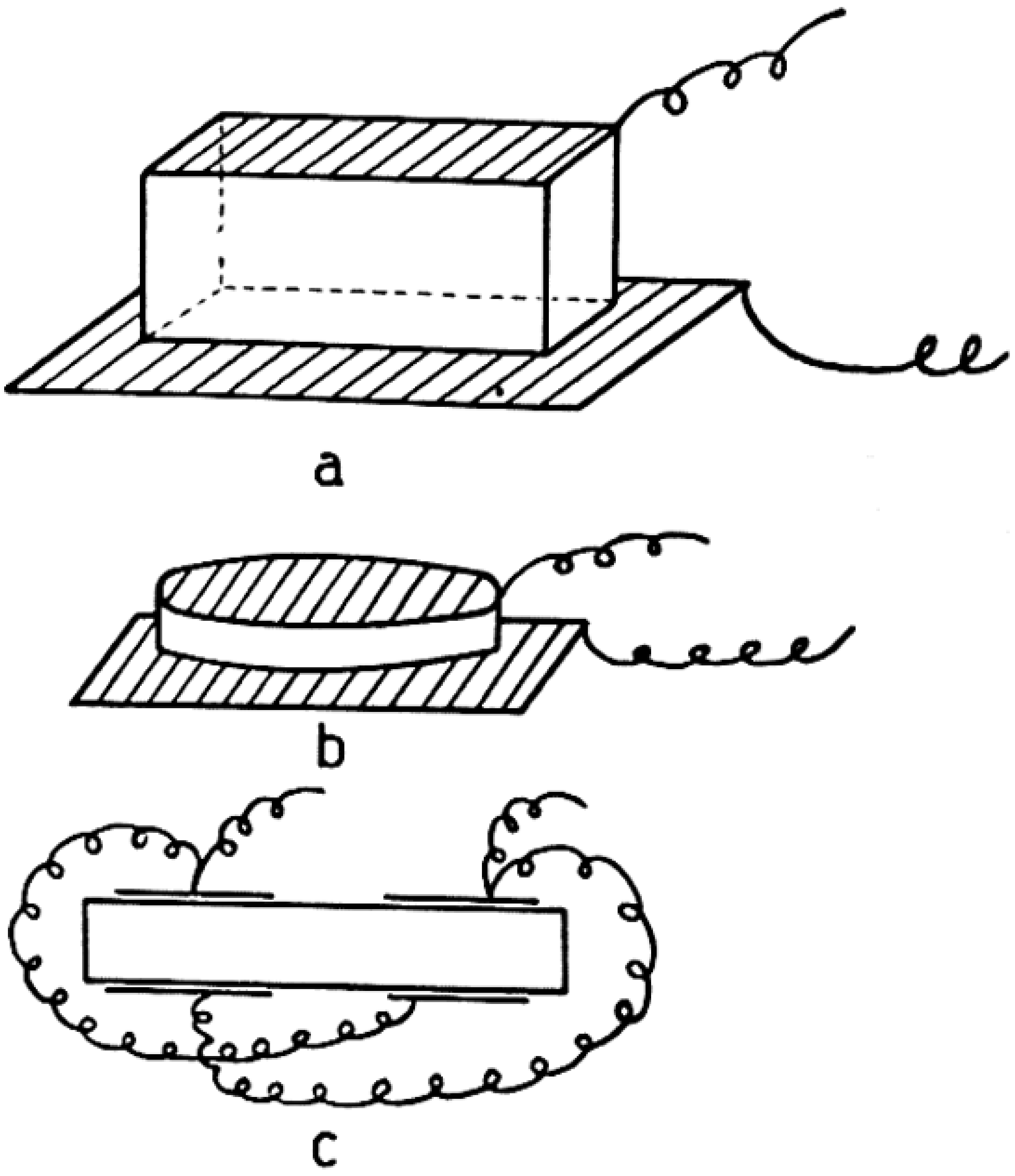

Fig. 3. Electrode Positions for Quartz Oscillators; (a) and (b) Longitudinal, (c) Torsional Modes

As the oscillatory potential surges from one pair to the other, the upper end is rotated first one way and then the other in relation to the lower end, so twisting the specimen. Torsional oscillations are of use in propagating shear waves into liquids (see Chap. VI), for the upper and lower surfaces of the quartz move parallel to themselves in oscillation.

3. Mounting of Quartz

The next practical aspect to be considered is the mounting of the cut slice. Slabs may conveniently rest on polished brass or stainless steel plates and carry an upper electrode of the same material but of lighter gauge. The latter may rest freely on top of the quartz, being restrained from falling off by having four holes near the corners a loose fit over four ebonite posts stepped into the lower plate. Alternatively the two electrodes may be held at a fixed distance apart slightly greater than the thickness of the quartz so as to leave an airgap of the order of one millimetre in thickness at the top; this is found to promote good oscillation in certain crystals (Fig. 4a). Again, there are two schools

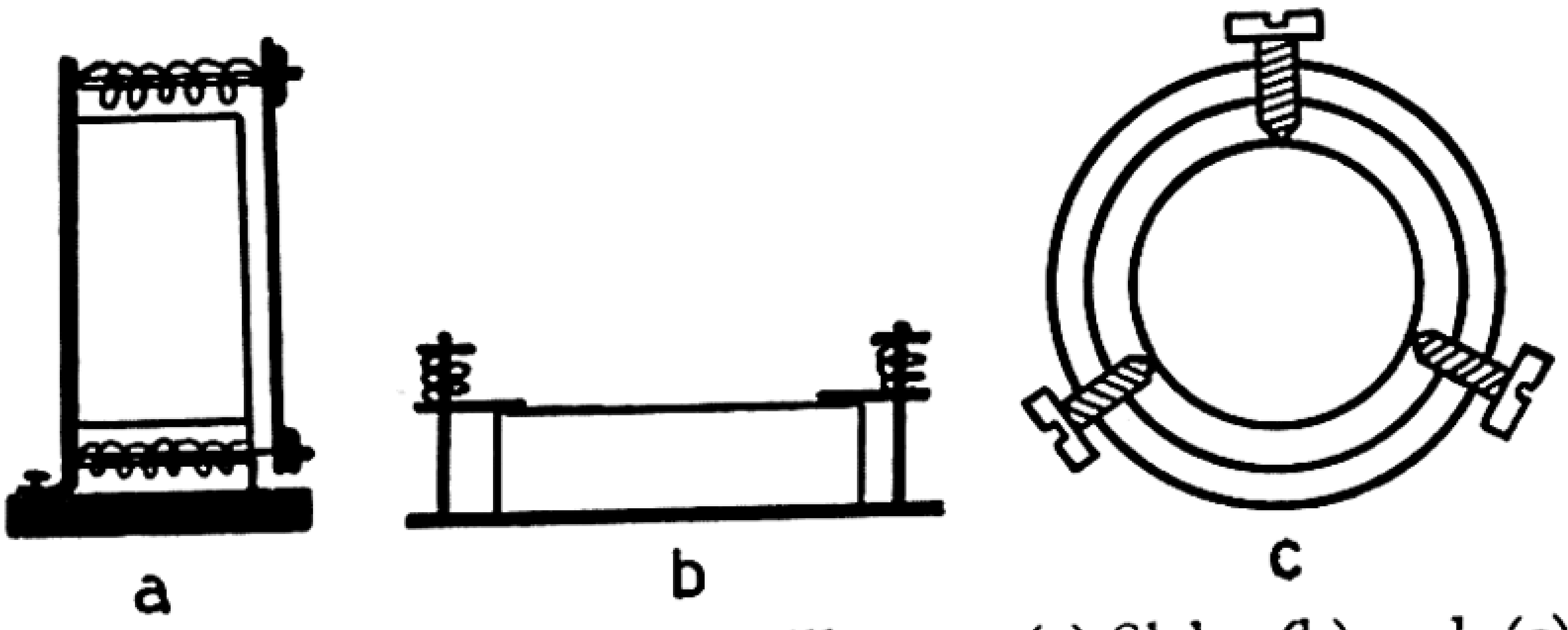

Fig. 4. Mountings for Quartz Oscillators; (a) Slab, (b) and (c) Disc

of thought in regard to the mounting of discs. Some, including the author, metallise the faces and let the disc rest on a block of metal, usually lead, carefully levelled and planed, to provide the earth connection in the oscillatory circuit, while a light catswhisker is fixed by Wood's metal to the — otherwise unencumbered — top surface (*cf.* Fig. 3). It is possible to make the underpinning plate take its part in the oscillation if it has the correct impedance and thickness (*vide* Chap. VI) by cementing it rigidly to the underface. This leads to some economy in quartz for the lower ultrasonic frequencies but such a sandwich is less efficient as a generator of waves in the ambient medium than one made entirely of quartz.

McGrath and Kurtz [13] describe another type of holder suitable for causing the quartz to radiate into a liquid electrolyte. The radiating face is separated from the latter, being enclosed in a thin rubber bag. The bag is filled with non-conducting liquid, *e.g.* alcohol, so that there is a progressive matching of impedance in the series; quartz, alcohol, rubber, electrolyte. Thus the radiation is led efficiently from the first to the last member in the line.

Others prefer an airgap *beneath* the disc. They press it by means of a light spring against the upper electrode in the form of a ring of diameter slightly less than the disc itself (Fig. 4b). The upper face then need be metallised only under this ring, and if the latter is soldered at its outer circumference to a hole in the metal base of a container, liquids placed therein may include conducting solutions without fear of shorting the electrodes. (In the type of mount shown in Fig. 3b the crystal must be sunk to the level of its upper face in a nonconducting liquid, heavier than the experimental liquid, if the latter is a conductor.)

For efficient conversion of electrical into ultrasonic energy, the depth of an airgap above or below the crystal is rather critical since compressional waves are set up in it and in returning react upon the crystal's vibrations (*vide* Chap. II), and this reaction will in turn be influenced by the temperature of the air within. For this and other reasons the author prefers the first mount without a gap, which may be adapted if need be to horizontal radiation by disposing block and crystal on their sides, a slight saucer of the disc diameter being first cut in the former into which the crystal is lightly pressed by a leaf spring touching the upper electrode.

A disc may also be gripped from the sides at three points insulated from the sputtered electrodes (Fig. 4c).

Quartz and most other piezo-electric crystals cannot run at high temperature efficiently, as the Curie constant diminishes and vanishes altogether at about 500 °C in quartz. The actual temperature coefficient of frequency, determined by the expansion and change of velocity of sound in quartz is small, of the order $5 \cdot 10^{-5}$. Such a small coefficient is not of much moment since in use the frequency of oscillation will be continually checked (*vide infra*), but by cutting at oblique angles with regard to the axes it is possible to eliminate the effects of temperature on frequency or to avoid elastic coupling between modes of vibration having nearby frequencies, another defect of certain "cuts" which results in unstable operation (*vide supra*, Straubel cut).

4. Circuits to Maintain Piezo-electric Oscillators

Circuits may be grouped according to whether the source is to be used

(a) to generate ultrasonic power,
(b) to measure propagation constants.

In this book we are mostly concerned with the latter type, but regard must be paid to the fact that more power is required when the source radiates into a liquid than into a gas. A further subdivision may be made, according to wether the source is an oscillator in the sense that it controls the frequency of the circuit in which it is located, or a resonator in which it is driven by a circuit in unison with it.

We shall now give specimens of three working types:

(a) resonant drive type (HARTLEY)
(b) self-maintaining type (PIERCE)
(c) push-pull type.

A serviceable specimen of each class is given and there follow a few general remarks on their operation and suitability for various experiments.

A later figure (27a) shows the much-used PIERCE[14] circuit with the crystal in its original position between grid and plate. In the modification due to MILLER (Fig. 5) the crystal is in parallel with the grid leak. This type has the advantage that no precise tuning is necessary. If the tank circuit has a natural frequency somewhere near that of the quartz, a slight mechanical disturbance of the latter will set it in vibration at its own natural frequency, to which it "pulls" the circuit.

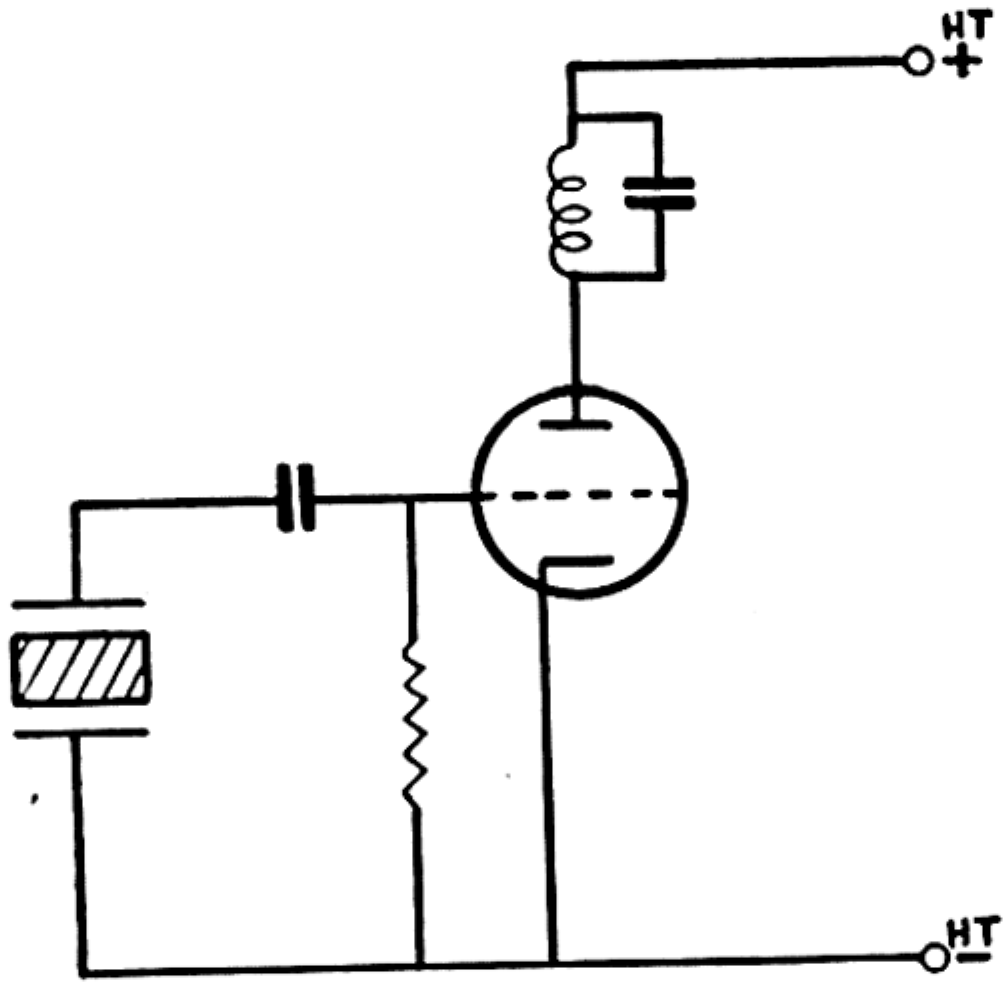

Fig. 5. Crystal-equivalent Circuit with Tuned Anode

A high L/C ratio gives a large harmonic content to the output. It is usual in tuning to bring C up to resonance from zero. When oscillation starts the d.c. current shown by the milliammeter drops more and more until when C is made too large the oscillations, which have then reached their maximum amplitude, suddenly cease.

Best results in the PIERCE-MILLER circuit, which is preferred for the higher crystal frequencies, are obtained with a valve of high amplification. Its function is to provide negative resistance to counteract the positive resistance in the crystal's impedance while it oscillates. The power output can be increased by shunting the crystal with a high-frequency choke and grid bias battery, the value of the latter being rather critical.

A pentode may be substituted for the triode shown in the figure.

It is advisable to use a low-power valve and high L/C ratio. In use this circuit is usually required to indicate, by the fall in the reading of the milliammeter in the plate circuit, the amplitude of the alternating current in the valve which in turn is taken to be proportional to the amplitude of oscillation of the piezo-electric source (see p. 77).

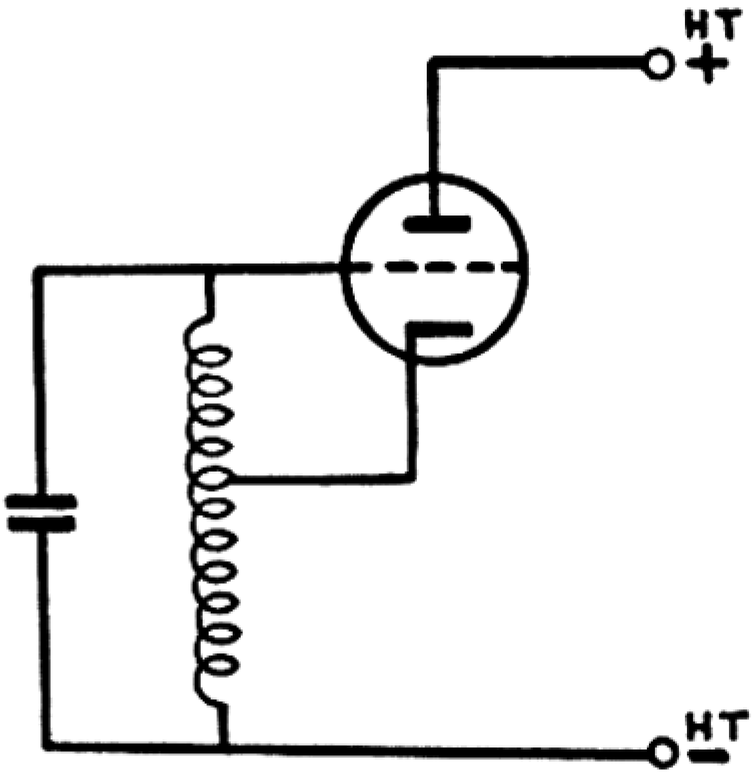

Fig. 6. Hartley Circuit

Though this method of measuring the crystal amplitude may be quite accurate, the milliammeter may on occasions be replaced for calibration purposes by an instrument which directly reads the alternating power reaching the crystal; such instruments are the thermo-milliammeter and the vacuum thermo-junction coupled to a sensitive galvanometer. Great care is, however, required in the use of these as, should an excess over the normal working current suddenly arise, they will inevitably be burnt out before a fuse or relay can protect them.

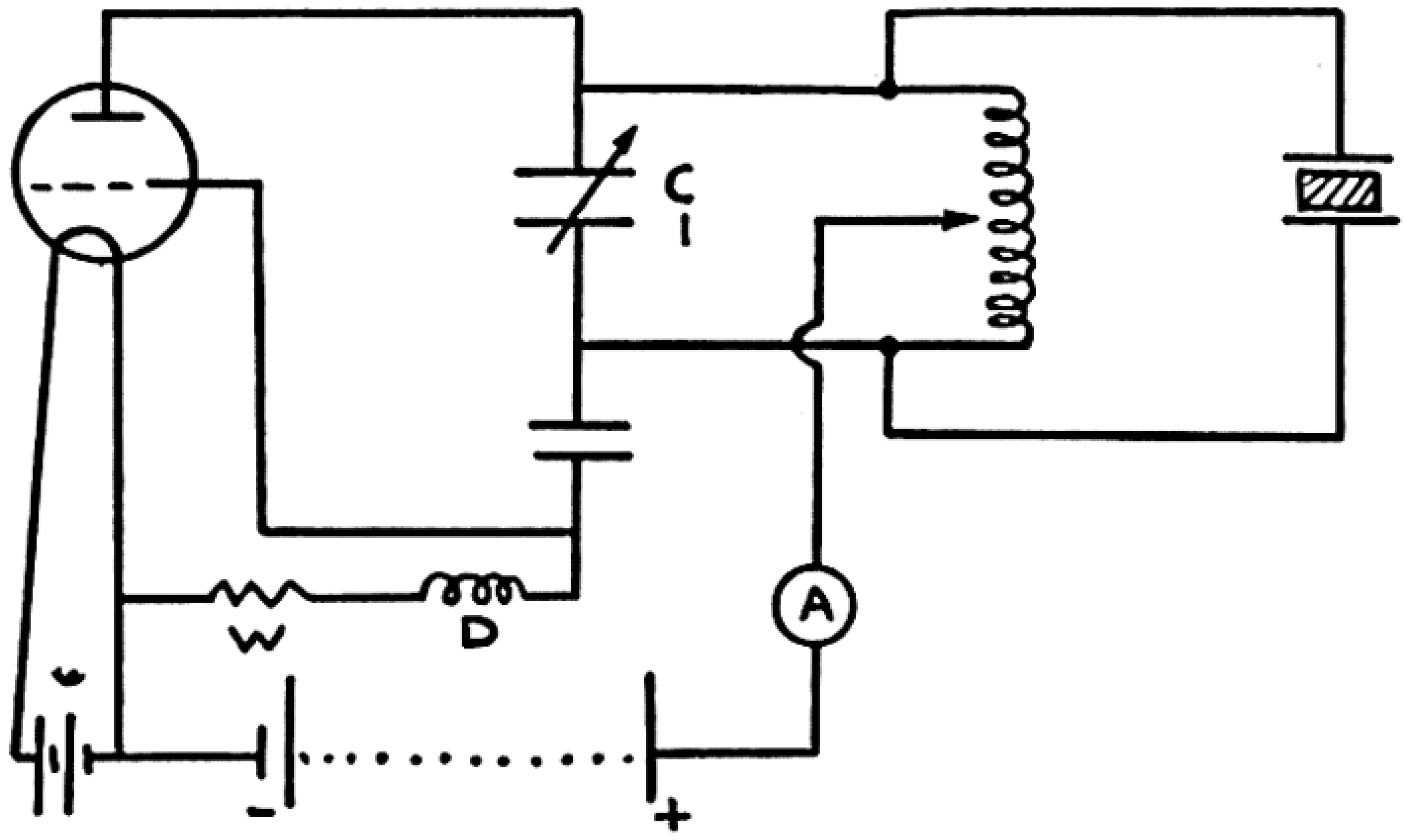

Fig. 7. Hartley Cicruit Driving Crystal

The Pierce circuit is less suitable for driving a crystal that radiates into a liquid owing to the load provided by the latter. The Hartley circuit (Fig. 6) in which the tank circuit is precisely tuned to the fundamental or a harmonic of the quartz resonator can be used for radiating ultra-

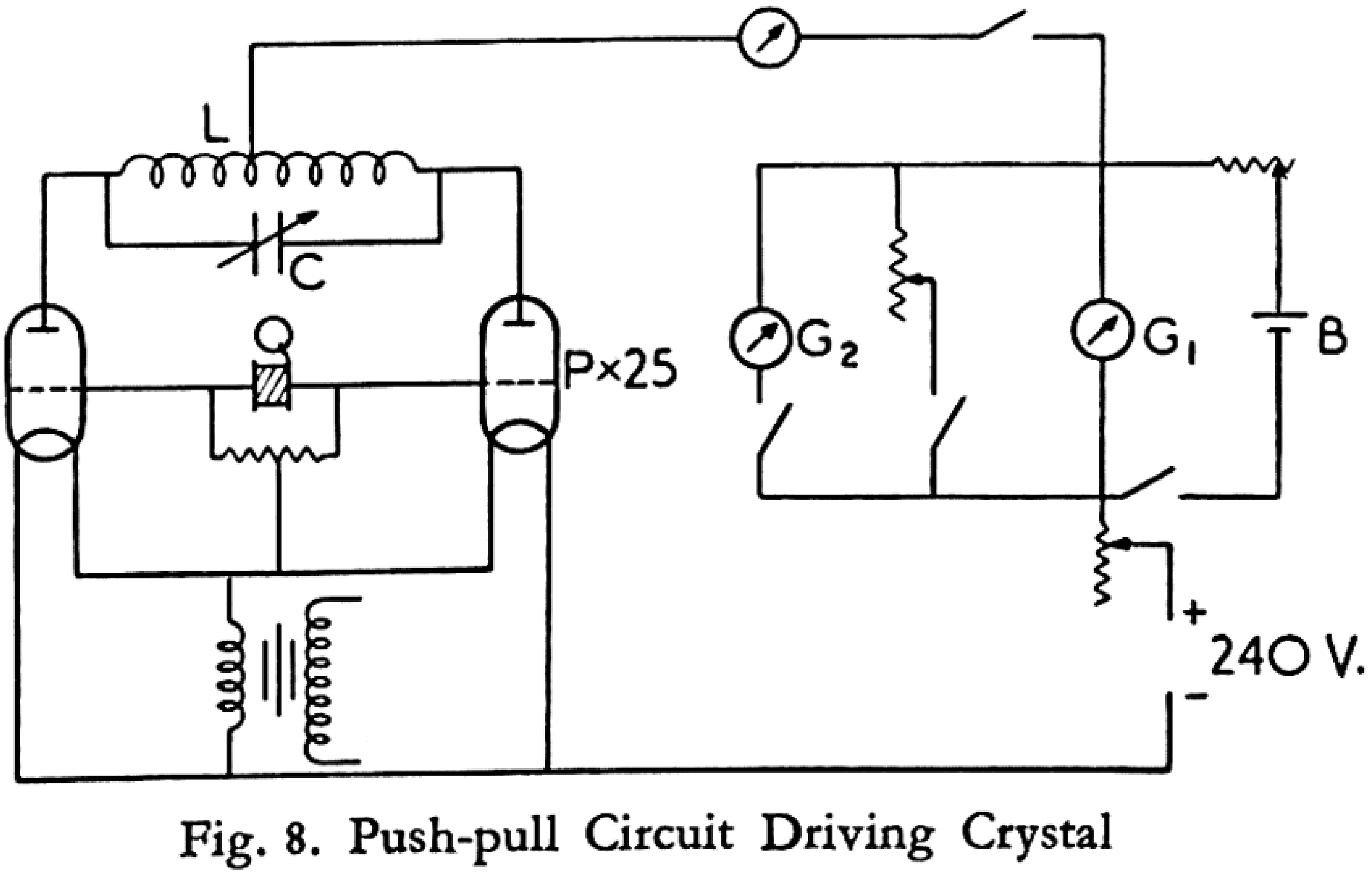

Fig. 8. Push-pull Circuit Driving Crystal

sonics into solid, liquid or gas. Fig. 7 shows a simple low-power type with the filament centre-tapped into the inductance of the tank circuit. The quartz may appear directly on the inductance as shown or be transformer-coupled to the circuit. Finally, Fig. 8 shows a typical push-pull circuit. In both this and the HARTLEY circuit, trials must be made of the best setting for each frequency of the position of the "centre-tap" to the induction coil to give good output.

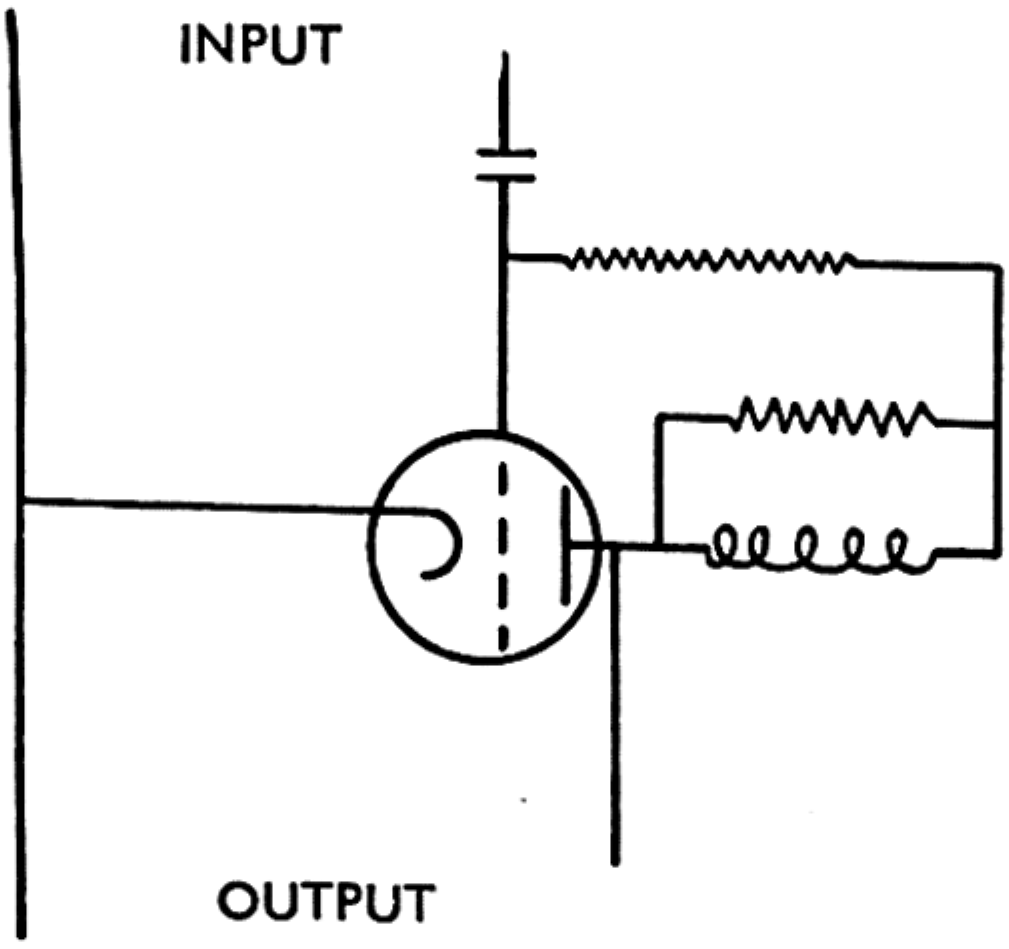

Fig. 9. Square-Wave Generator

For certain ultrasonic experiments, it is desirable to "pulse" the source, *i.e.*, to operate it intermittently for periods of the order of microseconds. BIQUARD and AHIER [15] first did this in laboratory measurements though it had been common in echo-sounding technique since the first world war. A square wave generator (Fig. 9) applies exciting potential to the crystal at regular intervals, making it emit a short train of waves at each epoch. The arrival of the square wave at the gas-filled valve, which is

References pp. 30–31

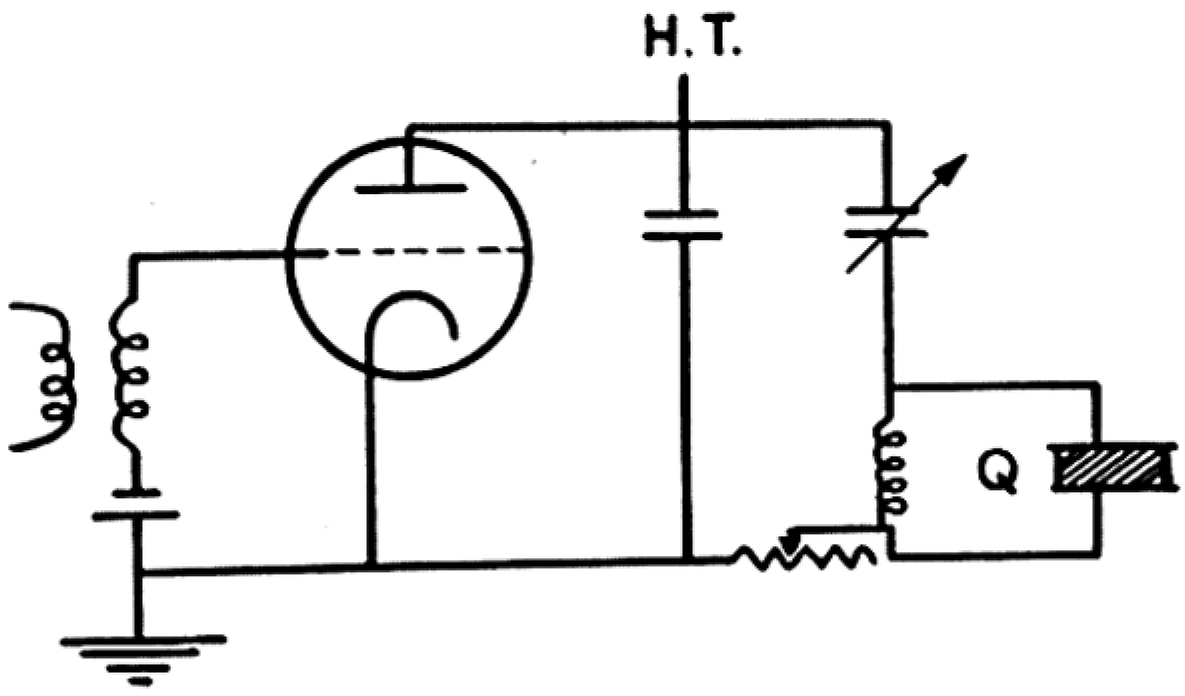

Fig. 10. Pulse Circuit

normally so biased that its output is insufficient to operate the quartz, "unblocks" it and provokes the crystal into activity for as long as the summit of the square wave lasts (Fig. 10).

5. Impedance of Crystal Oscillator

The equivalent circuit of the crystal in piezo-electric oscillation is shown in Fig. 11. Here L and C are respectively the equivalent inductance and capacity of the crystal, R its radiation resistance (which depends on the superficial area of the quartz and the nature of the ambient medium), C_1 is the total capacity between the electrodes, including that of the electrodes and plating, if any. The resonant pulsatance ω ($= 2\pi \times$ frequency) is given by $(LC)^{-\frac{1}{2}}$. Further, the ratio between the capacitance between the plates and equivalent capacity is constant. The resonance is very sharp and is expressed by the quantity $Q = 1/\omega CR$, and so is a function of the loading by the medium.

In quartz, the equivalent inductance is very small in the megacycle range but may be as much as 100 henries at the lowest frequencies; *C* is of the order of 10^{-6} microfarad. The high *L*/*C* ratio gives the high *Q* and so an inexorable frequency to quartz.

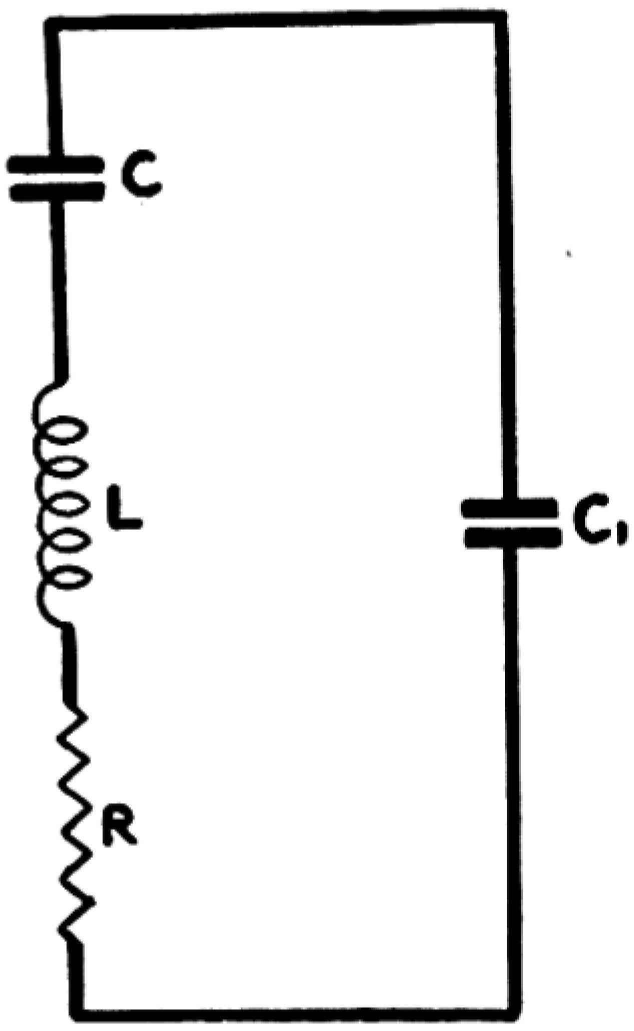

Fig. 11. Equivalent Circuit to Quartz

This circuit was first suggested by VAN DYKE. The *Q* of the quartz can be derived from a measurement of its resistance at resonance, but is indicative of internal losses only if it is not radiating into a fluid medium or energising a solid body in contact with it. The radiation resistance and so, the total impedance, of the source is affected by the radiation which it emits or receives. As we shall see later, the reaction on it forms a common way of determining the propagation constants (for ultrasonics) of the ambient medium.

One way of estimating this reaction is to measure the electrical impedance of the emitter in various circumstances.

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The corresponding mechanical factors: stiffness, inertia and resistance can then be deduced. The impedance of the crystal may be measured by building it into a high frequency Wheatstone Bridge. Fig. 12 shows a bridge designed by Bell [16] for ultrasonic measurements. For a resonant frequency of 250 kc/sec, the fixed resistances are of order 10,000 ohms, the variable one (*R*) is made up of carbon resistances giving 15,000 ohms by steps of a hundred; the variable condensers of 100 cm maximum have graduated dials.

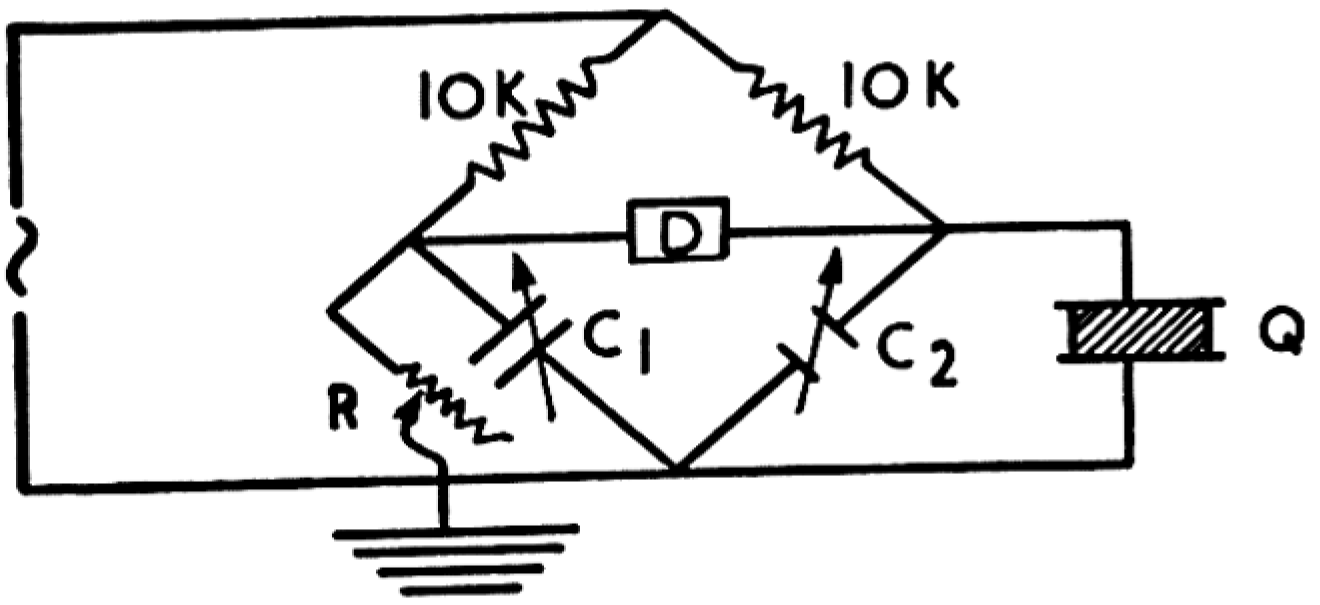

Fig. 12. Measurement of Crystal Impedance (Bell)

The input frequency is at first made to differ from the resonant frequency of the quartz and the bridge balanced by adjusting C_1 and C_2 with the connection to R open. R is then brought into the circuit and the balance thereby upset. The supply frequency and then R are successively adjusted until the balance remains unchanged on switching in R. The supply frequency is then equal to that natural to the crystal and the final value of R is its effective resistance.

The detector *D* is a tuned transformer followed by an amplifier and the input comes from a reliable valve oscillator. Considerable difficulties arise from slight wanderings of the output frequency of the oscillator and from "stray" capacities in *R*, necessitating careful shielding. By displaying on an oscillograph the out-of-balance current through *D*, led through a frequency-modulated system, any such wandering can be monitored and steps taken to combat it.

A *Y*-cut quartz is used to transmit shear vibrations into a contiguous solid. The longitudinal mode of an *X*-cut crystal can also couple with a shear along one of its faces, particularly if it is wide on the *Y* axis for its fundamental length in the longitudinal mode. This occurs when a stress in the direction of the length distorts the rectangular face of the crystal into a rhombus.

To sum up: with a piezo-electrically operated crystal of suitable size, working at its fundamental or one of its odd harmonics, one may generate longitudinal waves of compression in a solid or fluid medium over the range of frequency 20 kc/sec to 200 Mc/sec. Even harmonics cannot usually be produced and, if they are detected, are due to some assymmetry of the mounting or electrode disposition and soon degenerate into torsional vibrations. Using circuits of the Hartley or push-pull type, one may develop an ultrasonic power of 10 watts per sq. cm, it being understood that the delivery of power into a crystal is limited by its strength and that in a *gaseous* medium the figure quoted is unattainable without cracking the quartz. (This upper limit corresponds to one hundred million times the average sound output of a loud-speaker.) At a frequency of 200 Mc/sec the surface has a maximum acceleration of 100,000 *g*, well above the minimum required to produce cavitation in a liquid.

It has been our intention in this section to give the main facts about piezo-electric oscillators as far as they are involved as sources of ultrasonic radiation. Those who desire further information on the fundamental aspects of piezo-electricity are referred to CADY's monumental work on the subject (McGraw-Hill, 1946), from which the figures quoted in the penultimate paragraph are quoted, or to the more recent one by MASON (Van Nostrand, 1950).

6. Magneto-strictive Oscillator

Magneto-striction is the name given to the effect discovered by JOULE by which magnetic materials suffer a change in length, owing to a molecular re-arrangement, when the magnetic field in which they are placed changes in strength.

If a rod or ring of magnetic material is subjected to an alternating magnetic field parallel to its length, it can be set in oscillation at one of its natural frequencies.

The conversion of electro-magnetic into ultrasonic power is less efficient than in the electro-strictive sources owing to hysteresis which results in considerable heating of the material if one attempts to dissipate much power. Moreover, as the material cannot be excited in the form of a disc, the upper frequency limit is rather low. For this reason its application to the study of ultrasonic propagation is to be found in special sources in the form of a thin — solid or hollow — rod or needle. Here we may mention another form of source in which a number of metal stampings toroidally wound with coils radiate into and out of a metal horn. This is used for irradiating a large volume of liquid and for sounding in the sea by means of echoes.

The materials used in magneto-striction comprise the ferro-magnetic metals: iron, nickel, cobalt and their alloys. Of these nickel itself, glowray and nichrome give a moderate amplitude of oscillation and have a very low temperature coefficient of frequency. Monel gives more amplitude but has a slightly larger temperature coefficient. In the author's experience, monel is the best to use as an ultrasonic source, provided it is not allowed to heat up unduly.

Both Vincent[17] and Pierce[18] have devised suitable circuits to maintain the oscillations. Both recommend that

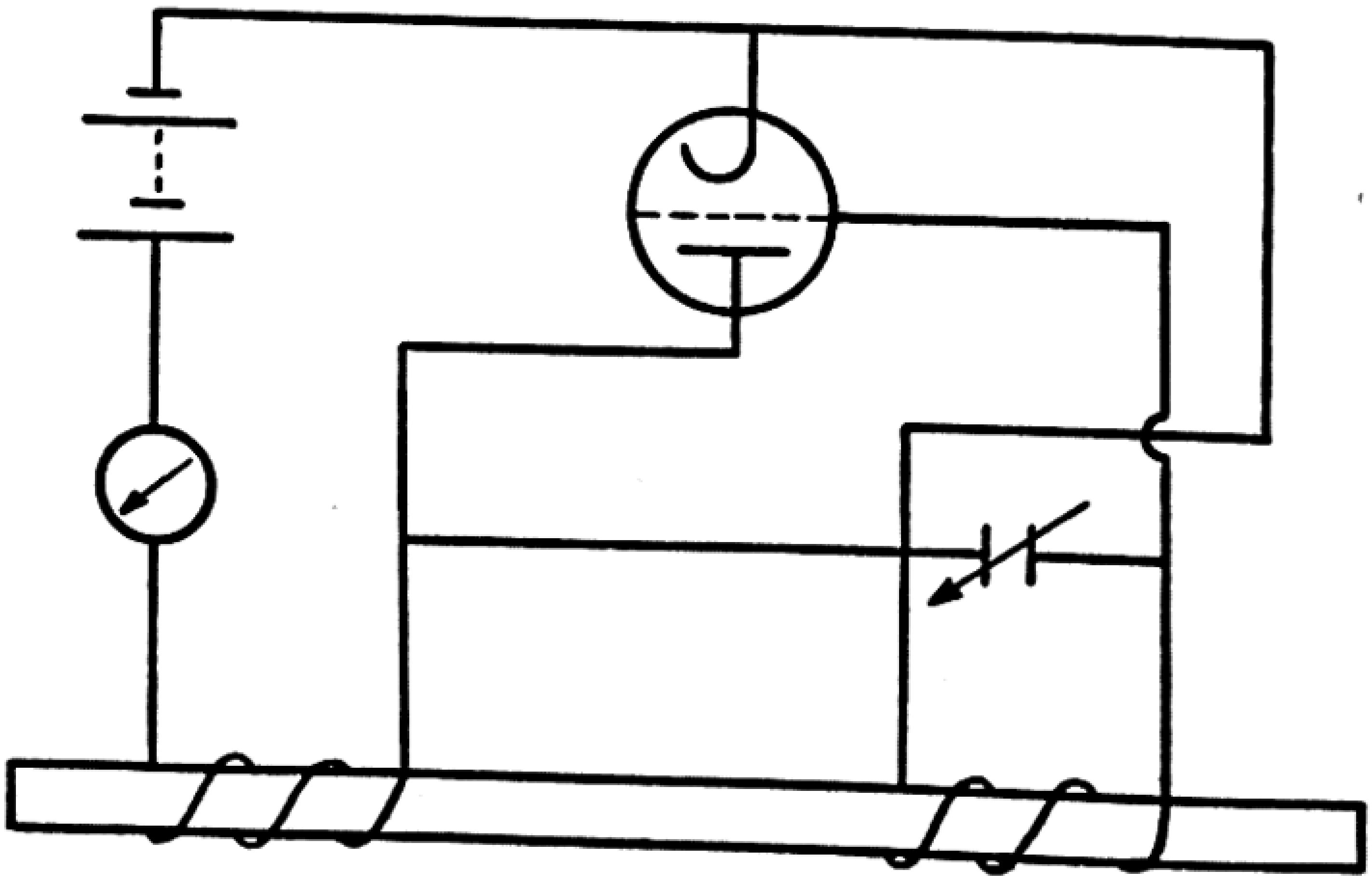

Fig. 13. Magneto-striction Generator

the rod should be polarised, *i.e.* have some permanent magnetisation before the alternating field is applied.

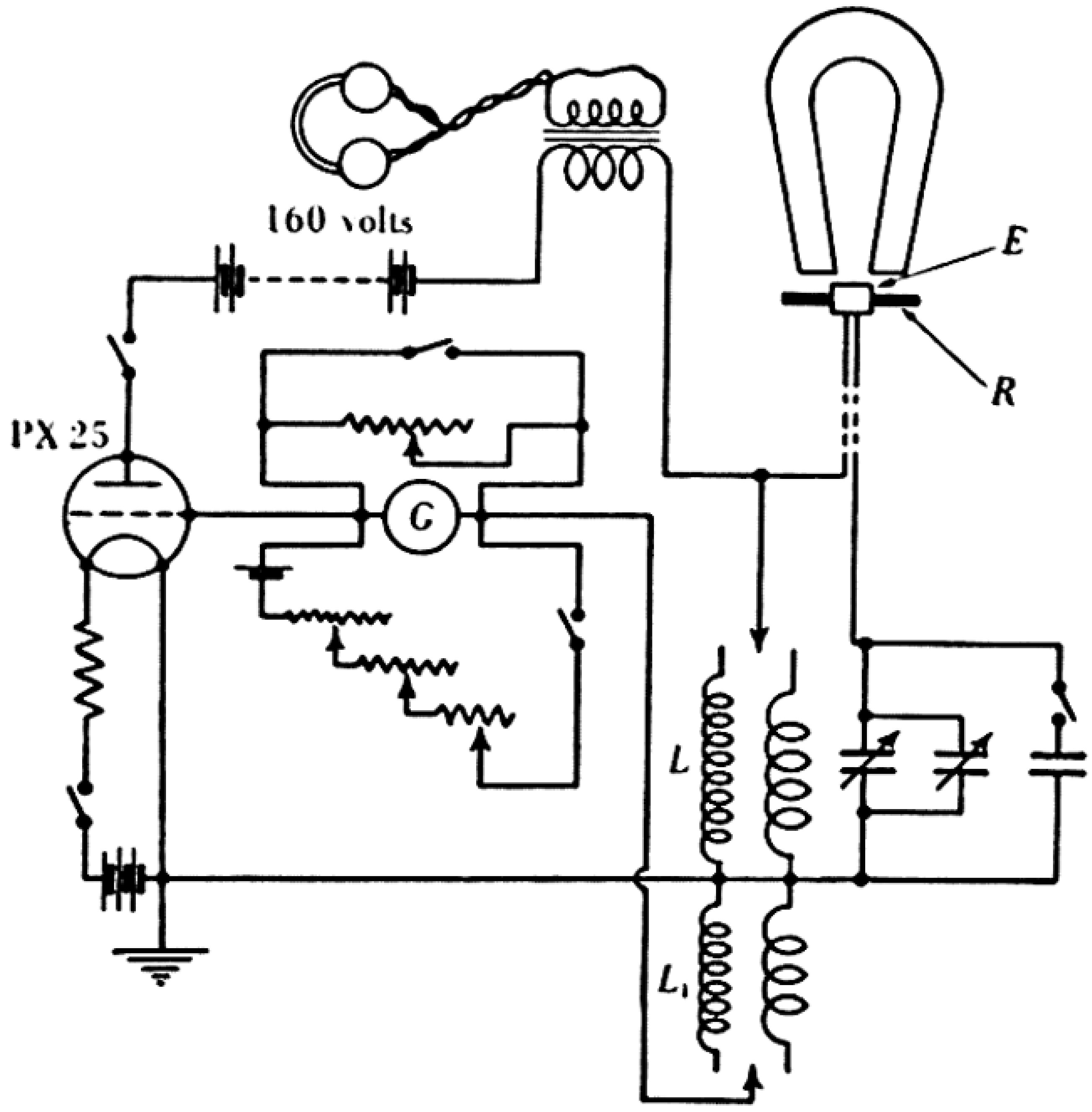

Fig. 14. Magneto-striction Circuit (MAY)

Fig. 13 is PIERCE's circuit and Fig. 14 shows VINCENT's circuit in a practical form. The coils L and L_1 are coupled so that the valve oscillates in the absence of the rod R, and the range of oscillation frequencies is made to include that of the rod under test. E is an exciting coil consisting of a few hundred turns of thin copper wire wound on a paper girdle round the tube. When the rod is inserted and the rotor of the variable condenser is turned slowly, the grid current changes in the manner described by VINCENT. As suggested by PIERCE, telephone receivers are used to detect the production of rod vibrations. Either a perma-

References pp. 30–31

nent magnet or an electro-magnet can be used to provide the polarizing field, which is a necessity for the functioning unless the material has permanent magnetism[19].

This type, with a monel needle as vibrator, is very suitable for generating ultrasonic waves into a fluid contained in a narrow tube, into which the source projects (*cf.* Chap. IV). The rather elaborate shunting applied to the galvanometer *G* shown in Fig. 14 is to vary its sensitivity, and to back off the steady deflection when slight changes in deflection are being sought.

7. Ferro-electric Crystals

A ferro-electric type of crystal is one with a natural polarisation in one or more directions over a certain temperature range. It exhibits hysteresis between applied field and charge developed and between mechanical stress and strain. Rochelle salt, the dihydrogen phosphates and barium titanate have these properties up to a certain temperature ("Curie point"). As a result of spontaneous polarisation, a strain proportional to the product of two fields is set up between it and the applied field, the so-called "second-order" piezo-electric effect. Barium titanate however, which requires *ad hoc* polarisation, shows an electro-strictive effect very much like that of magneto-striction in iron, involving re-alignment of molecules in the a.c. field.

Rochelle salt disintegrates at 55 °C. Between —18 °C and +24°C it becomes *spontaneously* polarised with a lag between polarisation and applied field; there is a maximum in this effect at 3 °C. If a voltage is applied to an *X*-cut crystal, it is distorted so that the rectangular face becomes a rhombus, but if the crystal length has been cut at 45° to the *Y* and *Z* axes, the crystal will expand along the length and contract along the width. This, the 45° *X*-cut, is the most common. The expansion bears constant ratio to the charge per unit superficial area.

Whereas Rochelle salt disintegrates to a powder when the humidity is low, because it then loses its water of crystallisation, ADP cannot do this.

Barium titanate, a multi-crystalline ceramic, polarised by an applied d.c. voltage can be excited in resonant vibration when a suitable alternating field is applied to it. Discs of the material can show radial as well as thickness response. There is also a thickness-shear mode when the applied a.c. field is perpendicular to the d.c. polarisation. The vibration is due to the second-order piezo-electric effect. The d.c. field causes molecules to line with the field; the a.c. field causes a change in the ferro-electric axis in the molecules, whereby more or less molecules are lined up. There is a pronounced hysteresis in these effects.

8. Electro- or Magneto-strictive Transducers

In both types of source we find electric or magnetic dipoles which, oriented by the applied fields, suffer large electric displacements *D*, or magnetic flux densities *B*, which in turn result in mechanical strain and a change in the size or shape of the body. Those which have the greatest ratio of mechanical to electric — or magnetic — strain will be most useful for our purposes. If σ is the strain, the relations are respectively:

$$\sigma = e\,D \quad\text{and}\quad \sigma = m\,B$$

where e is an electro-strictive and m a magneto-strictive coefficient.

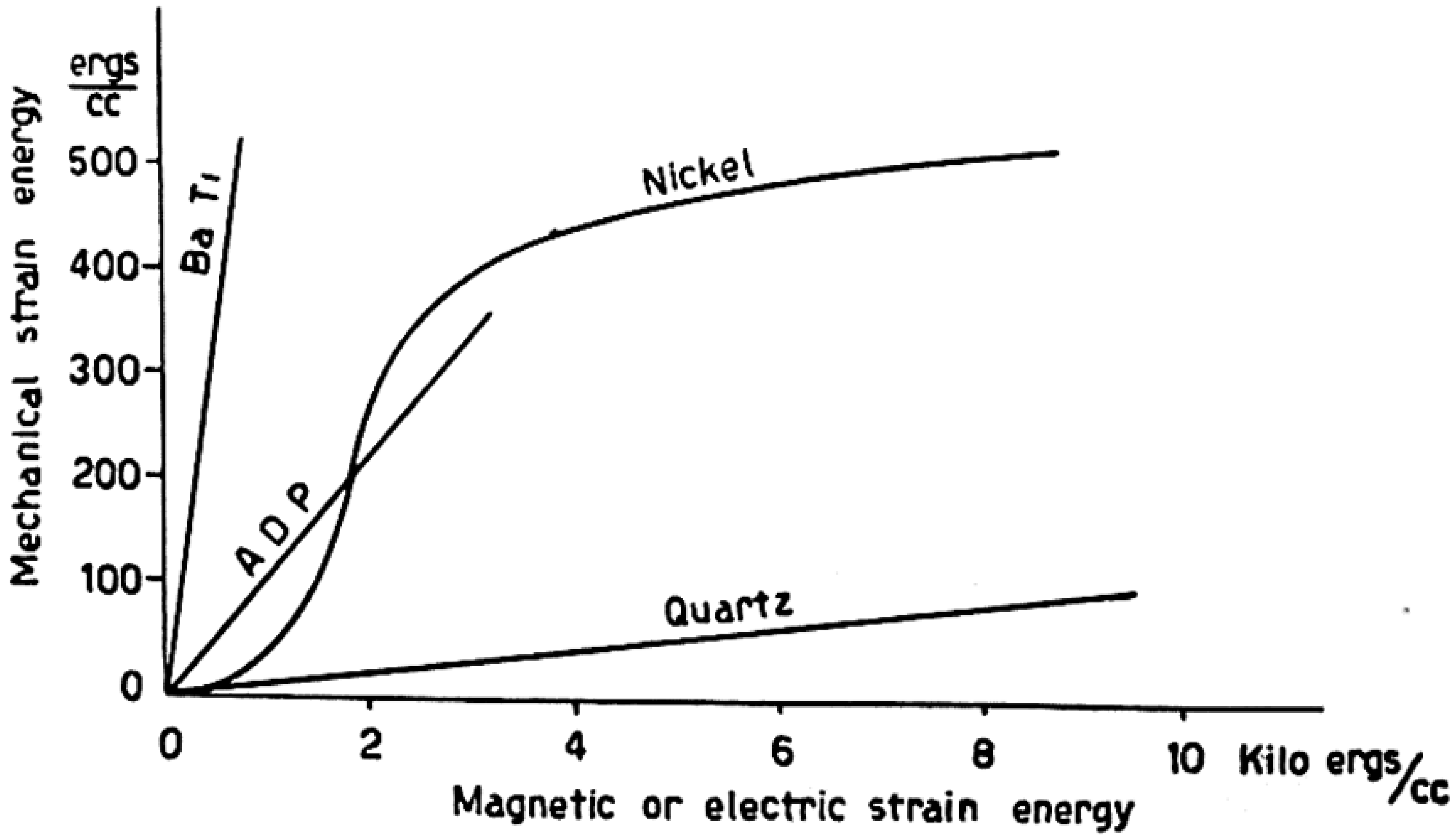

Fig. 15. Efficiency of Various Types of Ultrasonic Transducer (BRADFIELD)

In Fig. 15 (after BRADFIELD [6]) the relationship between these strains is shown for four types, a linear relationship for the three electro-strictive bodies (e constant) an S-shaped curve for the magneto-strictive nickel (m function of B). The superiority of barium titanate is very marked.

All these materials lose their special properties at a transition temperature * (< 500 °C), where there is a re-arran-

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* Called Curie temperature in magnetic materials.

gement of the crystal lattice resulting in a loss of polarity. Fig. 16 (also after BRADFIELD) shows the fall of the electro- or magneto-strictive efficiency as this temperature is approached for three substances. Barium titanate again shows to advantage at ordinary temperatures in maintaining its piezo-electricity at a high value till the temperature has reached 95 % of its transition point (120 °C). The internal losses are so small that its resonance curve is very peaked — it has a high "*Q*" — which means that we have to look for low-loss mounting and circuits.

The special properties of Rochelle salt will be discussed in Chapter VI.

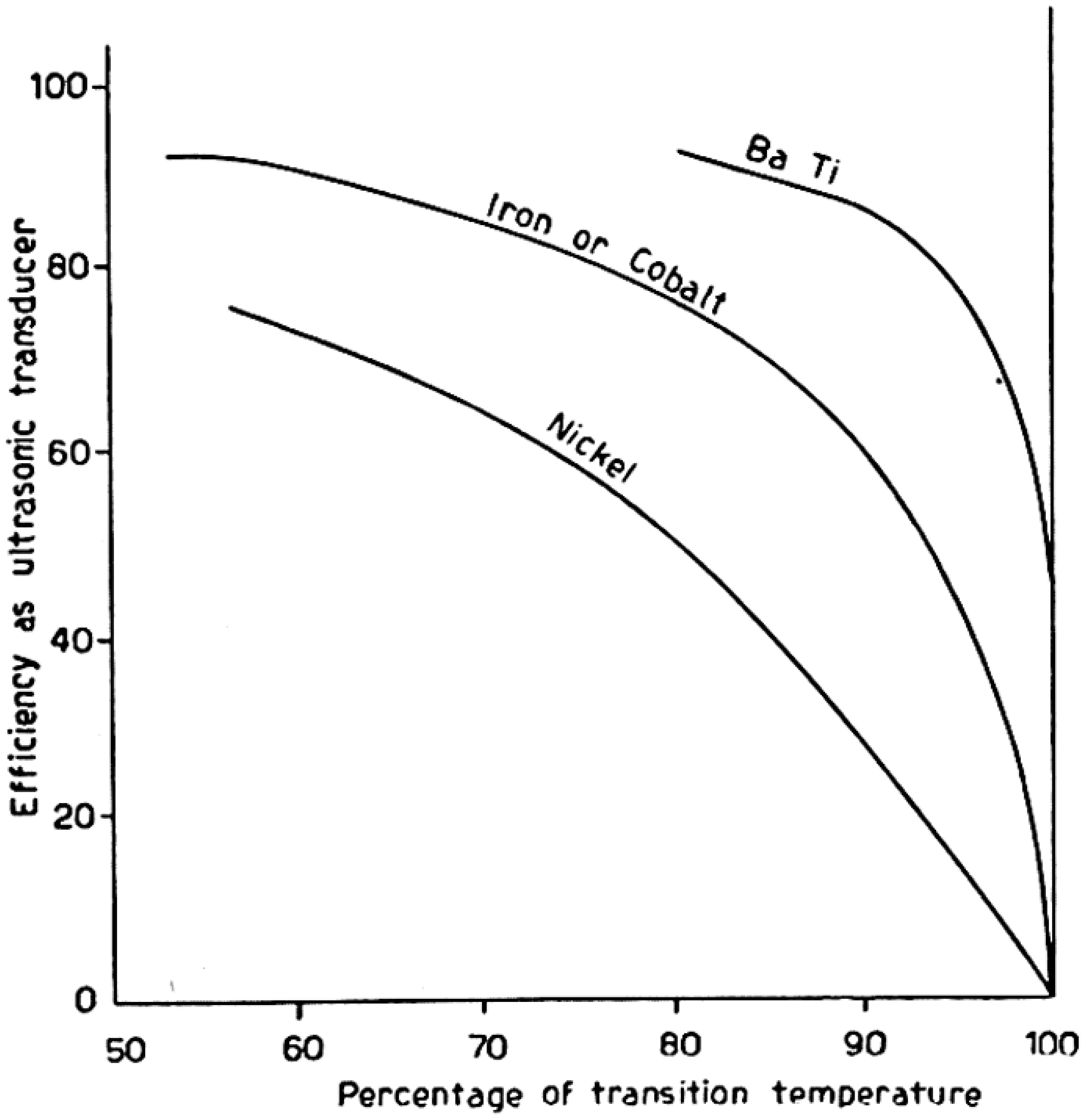

Fig. 16. Efficiency of Ultrasonic Transducer as Function of Temperature (BRADFIELD)

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CHAPTER II

METHODS OF DETECTION AND PROPERTIES OF ULTRASONIC RADIATION

The detection of ultrasonic waves as they irradiate a medium is possible by all the means commonly used for sonic waves except that the ear cannot be used. In this chapter we shall consider effects in progressive waves only, leaving for the next chapter the stationary waves and the technique of ultrasonic interferometers in which they are employed. In particular, we shall show here how some of these detectors have given information about the ultrasonic field in the neighbourhood of the source, a very important factor in the light of the use made of radiation from such sources to gain knowledge of the molecular properties of the medium so treated.

The types of detector which have been used comprise:

A. Mechanical detectors: smoke, dust, droplets, films, flames, radiometers;

B. Electrical detectors: resistors, hot-wires;

C. Optical devices: shadowgraphs, schlieren and diffraction methods;

D. Microphones.

A and B are used in fluids, C in liquids and transparent solids, and D mainly in liquids. Not all of these are suited to quantitative measurement, but we shall concentrate on those which can be used with precision.

1. Smoke Method

This has especially been practised by ANDRADE and his collaborators. When light solid particles or liquid drops — such as constitute tobacco smoke — are introduced into the sound field of a gas, the particles take up the motion to an extent depending on their inertia relative to the gaseous molecules. The appropriate expression for the fractional amplitude of the "markers" so introduced was found by KÖNIG [1] and has been verified by ANDRADE [2] as:

$$\frac{\xi}{\xi_1} = \sqrt{1 + b^2} \quad \text{with} \quad b = \frac{2}{9} \frac{\varrho_1}{\varrho_0 \, \lambda \, a^2} \tag{1}$$

where ξ_1 and ξ are the respective amplitudes of marker and sound wave, a, ϱ_1 the radius and density of the detectors, ϱ_0 the density of the gas. From this it is apparent that very small particles must be introduced into the gas if this method is to succeed in the ultrasonic gamut, and evenso the correction factor quoted above must be calculated. For example if water particles of radius 1 micron (a likely size) are introduced, their motions will only approximate to the amplitude of air molecules if the wave-length is more than 10 cm. This condition limits the application to the

References pp. 66–67

lower ultrasonic frequencies. Moreover there is a tendency of ultrasonics to promote coagulation. The particles in a typical tobacco smoke are of radius about 0.1 micron five minutes after dispersal, but grow in mean size by coagulation.

The technique of this method is therefore to feed particles of known and uniform size into the field, to photograph them with a long enough time of exposure that their motions appear as streaks on the negative, and to gauge the length of these streaks under suitable illumination to deduce the amplitude of motion. The particles are sparsely distributed in order to avoid their coalescence. By turning off the source and letting them fall freely through the focal plane of a microscope their velocity of free fall and hence their size may be estimated, assuming Stokes' well-known law.

2. Behaviour of a Large Obstacle in the Field

(This discussion will be necessary to understand the action of the radiometer). Consider plane waves incident normally on a boundary between two media. Let the incident wave, moving in the direction of increasing x with velocity c be

$$\xi_1 = f(ct - x) .$$

The fractional increase of pressure over the atmospheric produced by the wave:

$$s_1 = -\frac{\partial \xi_1}{\partial x} f'(ct - x) = \frac{\dot{\xi}_1}{c} .$$

References pp. 66–67

Similarly, for the reflected wave: $s_2 = - \frac{\dot{\xi}_2}{c}$.

and for the transmitted wave: $s' = \frac{\dot{\xi}'}{c'}$.

At the boundary, we apply two conditions: (a) that the particle velocity normal to the boundary and (b) that the normal pressure due to the waves on the boundary, must each be the same in both media.

Hence

$$cs_1 - cs_2 = c's'$$

and

$$es_1 + es_2 = e's'$$

Where e and e' are the respective elasticities of the two media. This gives us the reflection coefficient, in the form of the relative pressure amplitudes in the incident and reflected waves:

$$\frac{s_2}{s_1} = \frac{e'c - ec'}{e'c + ec'} = \frac{\varrho'c' - \varrho c}{\varrho'c' + \varrho c}, \tag{2}$$

introducing the respective values of the velocity of sound, c and c', the square of which is the quotient of elasticity and density.

The product of density and velocity of sound is an important property of a substance and is known as its "characteristic or specific impedance", and in plane waves is a pure resistance independent of frequency.

We have, in the above treatment, assumed that the boundary separates two media, which each occupy a "semi-infinite" space. Corrections are necessary if the boundary

References pp. 66–67

is limited in the direction of the wave front and if one or both of the media are limited in the direction of propagation. Both these factors pertain to reflectors used in practice.

Rayleigh[3] obtained the form of the reflection coefficient for the case of a lamina of material of thickness d and specific impedance $\mathfrak{z}'$ separating two regions, characterised by $\mathfrak{z}$:

$$\frac{s_2}{s_1} = \frac{\dfrac{\mathfrak{z}'}{\mathfrak{z}} - \dfrac{\mathfrak{z}}{\mathfrak{z}'}}{\sqrt{4\cot^2\dfrac{2\pi d}{\lambda'} + \left(\dfrac{\mathfrak{z}'}{\mathfrak{z}} + \dfrac{\mathfrak{z}}{\mathfrak{z}'}\right)^2}} \tag{3}$$

The expression reverts to the simpler form whenever the thickness is an odd multiple of one quarter wavelength λ' in the material.

When the solid is so exposed to the normal incidence of radiation, it experiences a force which is equivalent to the energy arriving at its surface per second plus that in the reflected wave. For simple harmonic waves $\frac{1}{2}\varrho\dot{\xi}^2$ is the kinetic energy in unit volume at any instant. The energy arriving at the surface per second is $\frac{1}{2}\mathfrak{z}\dot{\xi}_0^2$. So $(\pi f\xi)^2\mathfrak{z}$ — integrating over a complete period — is the value of the force due to the incident radiation. For the reflected wave, we must add on a similar term multiplied by the reflection coefficient from equation (2). There is a correction to be applied for the diffraction which ensues when the reflector is comparable in size with the wave-length, but as the same problem arises in the diffraction from a radiating source we shall defer such discussion to a later point in this chapter. With an obstacle of similar density to the fluid, there may be a tendency for it to swing with the vibration, but we have already discussed this point in the preceding section.

3. Radiometers

We may use the principles laid down in the preceding section to measure the amplitude in ultrasonic waves permeating a fluid by the force which they exert upon an obstacle — usually a solid disc — on which they impinge normally. It is evident that we shall prefer an obstacle unmatched in specific impedance with the fluid medium, in order to have a large reflection coefficient and so enhanced sensitivity. (Incidentally the reason for mounting quartz emitters on lead or other heavy blocks or backing them by an air film of thickness equal to a quarter wave-length of ultrasonics is to get most of the energy returned from

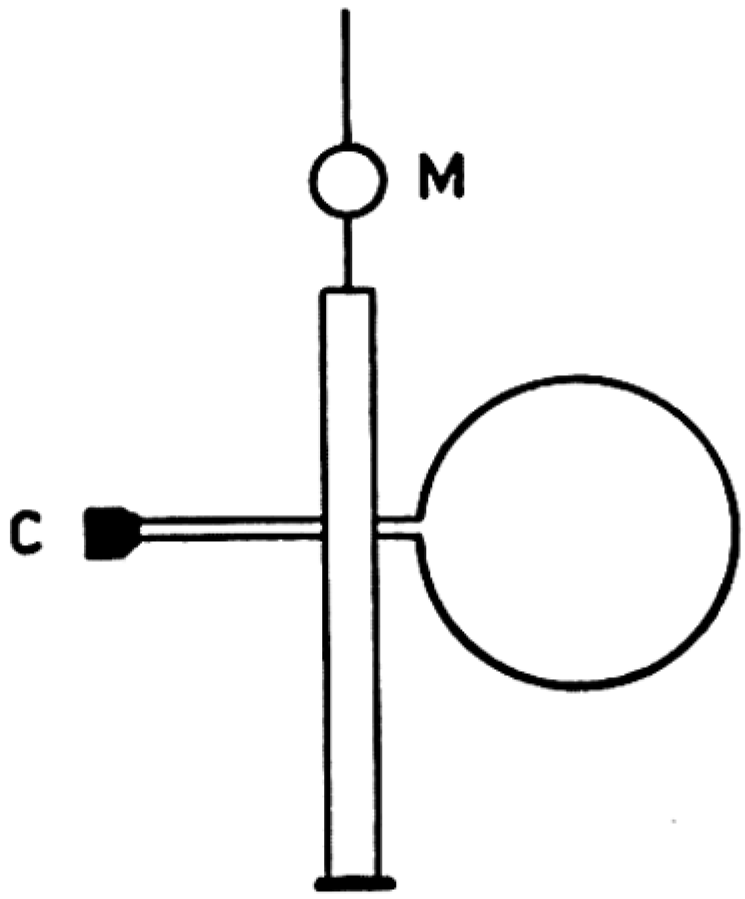

Fig. 17. Torsion Pendulum Radiometer

the metal interface and radiated in the contrary direction.)

BOYLE and LEHMANN [4] first used a disc suspended on a torsion fibre to measure intensities in a beam of ultrasonics passing through water. When the force acted on the disc to deflect it, it was restored by twisting the torsion head. Fig. 17 shows a suitable form of disc with mirror M attached to record deflections. They used lead discs of various thicknesses and verified the relationship contained in Rayleigh's formula (3). They also investigated the diffraction effect (*vide infra*), demonstrating that for a given setting of a disc, the deflection was a function of D/λ, D being the diameter of the disc. It should be pointed out that unless this ratio is small — which makes the instrument insensitive — the waves reflected back can interfere with the primary beam and possibly react on the source, so that the action on the disc must often be considered as that due to a system of stationary waves which may be set up between it and the source. With most discs the radiometer effect passes through cyclic values as the disc is drawn away from the source and may not give a true indication of the manner — usually exponential — in which the amplitude should diminish with distance in a progressive wave [5]. SÖRENSEN [6] measured the radiation pressure on a disc held on a balance, while other investigators have used a sphere as radiometer, claiming that it reflects little energy directly towards the source from its curved surface but most towards the walls where it can be absorbed by a covering of suitable impedance. Naturally, problems of inertia and diffraction arise similar to those mentioned in connection with the disc, but these radiometers are usually intended for comparative readings, so that only factors which vary with distance are of importance.

Radiation pressure measurements on fluid detectors are less used. They possess the sole advantage of very small inertia. For instance, a soap film can be stretched across a wire frame and exposed to the radiation — in a gas, naturally. The detector swings with the waves in the gas and its amplitude may be observed under a microscope, especially if dust particles in the guise of *mucae flotantes* are introduced into the film.

One can also use the sensitive flame as indicator but it is difficult to turn this into a device susceptible of quantitative indication [7].

If the waves traverse a liquid towards a free surface or towards the boundary between two immiscible liquids, radiation pressure distorts the surface and sets up crispations upon it. This effect depends on the relative densities of the two fluid media concerned and upon the depth of the source below the interface, in terms of wave-lengths.

None of these radiometric devices is so suited to delineate an ultrasonic field as those described below, mainly because, to be sensitive they need to be large, but to avoid distortion of the field they need to be small — and then they diffract. The best radiometer is probably the small sphere, with means of preventing the scattered and reflected rays deriving from it reacting on the source.

4. Electrical Detectors

These are of two types, (a) thermometers (b) anemometers.

The compressions and rarefactions taking place in a fluid result in temperature changes, in accordance with the adiabatic law. The temperature amplitude is small, of the order of a tenth of a Centrigrade degree, so that sensitive thermometers are needed to detect it. The feat was first accomplished in sonic waves by NEUSCHELER [8] who employed a Wollaston wire of 0.001" diameter and observed the oscillatory change of resistance. A similar device was used for ultrasonics by MALOV while JOHNSON used sensitive thermocouples; but one cannot hope to convert the readings into temperature amplitude by the use of a static calibration, as the wire cannot respond to the high frequency fluctuation. One must calibrate in known displacement amplitudes at the frequency in question and, in the light of this dynamic calibration, convert readings in the sound field to be explored.

TUCKER and PARIS [9] first used the cooling of a hot-wire in a sound wave as a measure of velocity-amplitude in their hot-wire microphone and this device has been extensively used by the author [10] for exploring ultrasonic fields and in the ultrasonic interferometer (see Chap. III). A fine platinum or nickel wire so exposed suffers an oscillatory change of temperature and so, of resistance, which is only representative of a fraction of the ultrasonic amplitude, owing to the lag in attaining equilibrium with a rapidly varying velocity. For the same reason this ripple is superposed on a steady drop of temperature, or of resistance. One can amplify the response with such bias that this lag is compensated; this, by means of a resonant circuit. The steady drop, at any *set* frequency, can however be related to the ultrasonic velocity amplitude, which is a more convenient way of using the instrument. Fig. 18 shows a calibration curve at 98 kc/sec in two gases for a nickel wire of diameter 0.001″ fed by a current of 0.2 amp. The calibration curve was obtained in this wise: The hot-wire (½″ long) was mounted on the thin prongs of a metal fork in a chamber in front of the quartz oscillator, the wire being horizontal

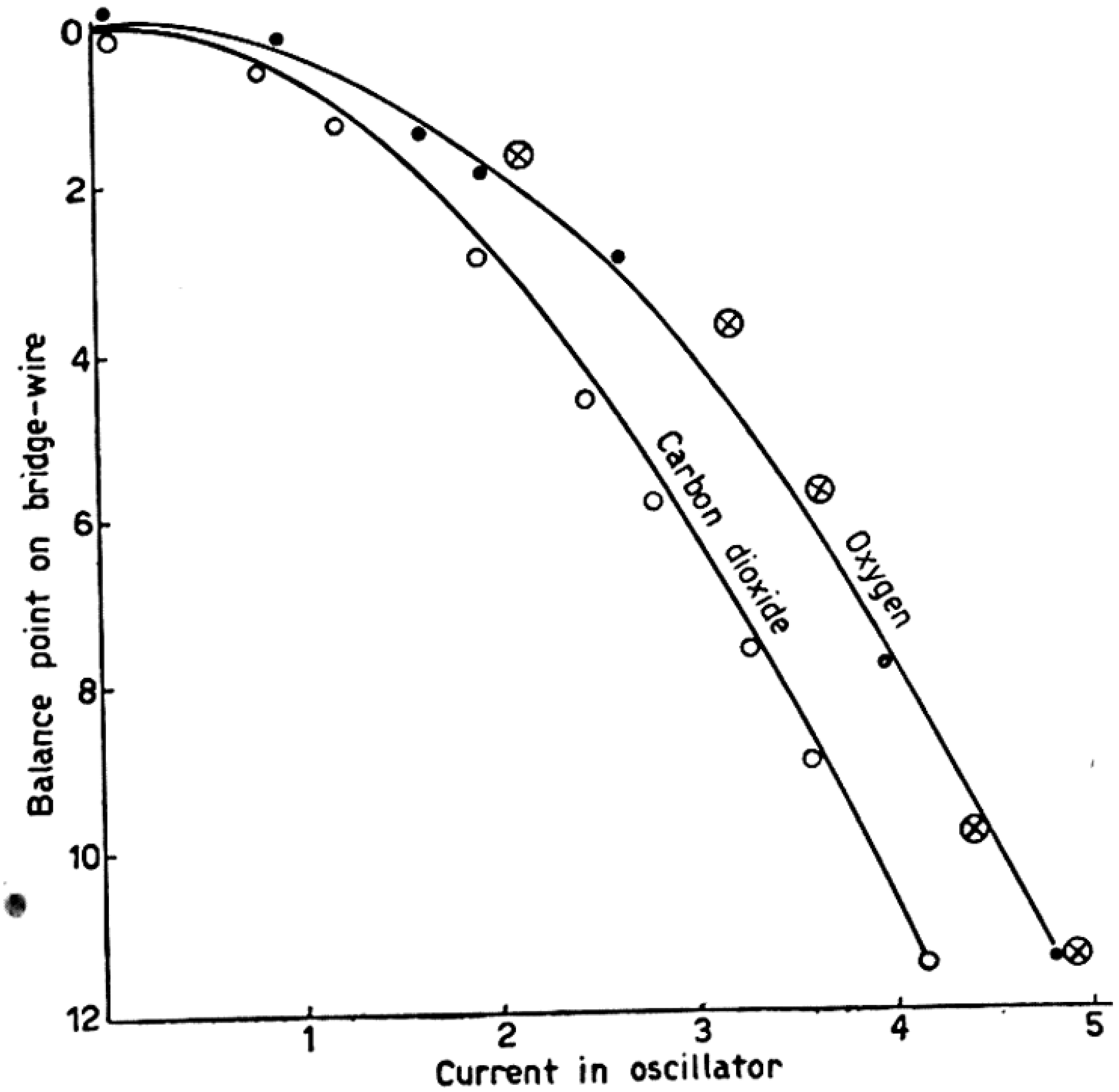

Fig. 18. Hot-Wire Calibration in Two Gases

References pp. 66–67

and parallel to its face. The alternating current supplied to the crystal was measured directly across its electrodes by a thermo-galvanometer at the same time as the steady drop of resistance of the wire, on a sensitive Kelvin bridge. It was assumed that the piezo-electric amplitude of the quartz was proportional to the potential across its electrodes (see Chap. I). The resulting curves in two gases are shown in Fig. 18 and correspond in shape to those obtained at low frequencies. Except at low excitations, the change of resistance with amplitude is linear. One can, in fact, linearise this curve completely, over the range at which one is likely to use it, if one applies the change of potential across the wire to the grid of a variable-mu valve and uses the plate current from the valve as a measure of amplitude, as RAILSTON and the author have done. Fig. 19 shows the circuit applied to a VS 24 or W 21 valve, the grid bias being so adjusted that no anode current flows while the wire retains

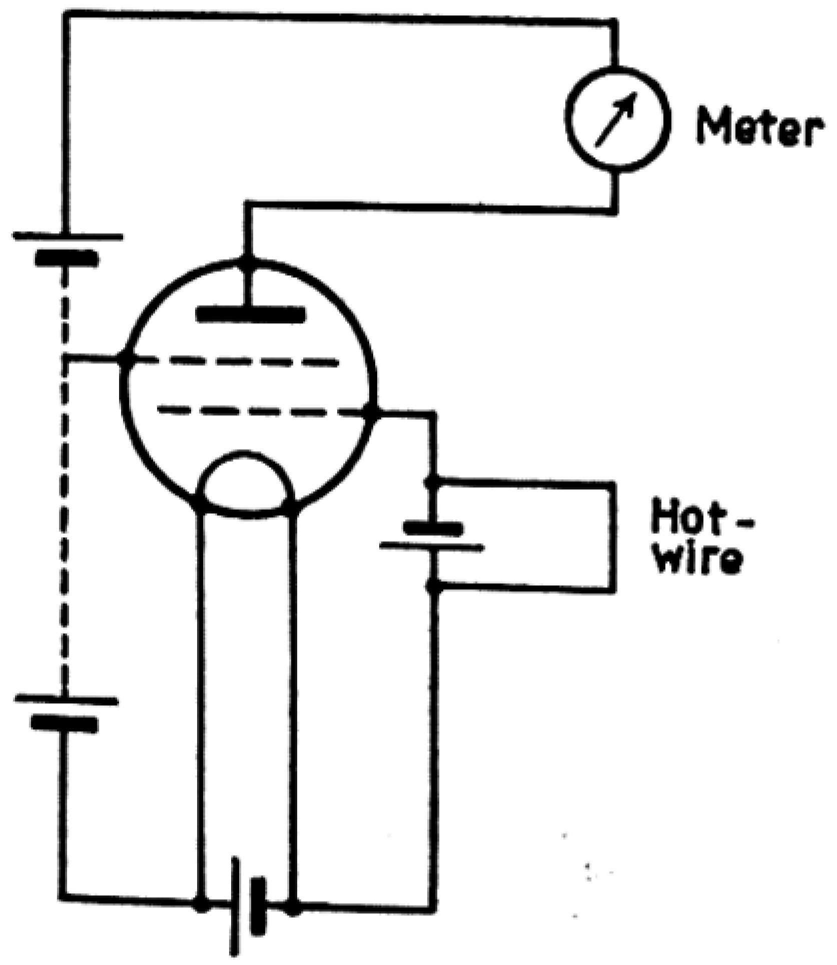

Fig. 19. Hot-Wire Detector with Linear Response

its hot resistance, corresponding to zero velocity. The hot-wire may also be used in liquids, as we shall see, although with some loss of sensitivity as compared with its use in a gas. Later in this chapter and in the next, examples of its use will be given. In a gas irradiated with ultrasonics it is in fact very sensitive and it is desirable not to use a large heating current. For the calibration cited, the temperature excess was about 50 °C, but in the stationary waves which we shall consider in Chap. III an excess temperature of half this value suffices.

5. Optical Methods

In this section will be discussed those methods by which an ultrasonic field may be delineated by passing a beam of light athwart the ultrasonic beam. There are several variants of this method, but they are all based on systems which, at the hands of TOEPLER [11] and DVORAK [12], had long been familiar tools of research in acoustics, when sonic beams traverse fluids. Fundamentally they rely on the fact that the fluid is compressed along a wave-front, and so the refractive index to light is there raised above normal in proportion to the change in density. This causes light which crosses such a front at right angles to be deflected from its forthright direction so that a shadow is cast on a screen or photographic plate at a distance. If the wave-front is spherical, the shadow is a circle; if it is plane, a straight line, and so on.

DVORAK used the sound pulses from sparks and photographed their wave-fronts as direct shadows, in this way. TOEPLER obtained good optical definition in his *schlieren* process, adapting the device which FOUCAULT had used for testing lenses. He brought the light from a concave mirror into the camera but intercepted it with a knife-edge pushed into the beam from one side near the focus. The plate in the camera then remains dark until some optical irregularity supervenes — such as may result from the passage of a compression in front of the camera lens — whereupon the pattern of the modulated light is cast on the plate. Both methods require the pressure amplitude in the wave-front to be large. This is easy to attain when the waves are shock waves originating from the passage of a projectile through the air at supersonic speed, but needs a fairly intense source if ultrasonics are in use. Both plane and spherical progressive waves may thus be cast in silhouette when they traverse a liquid, at anyrate near the source, and recently HUBBARD and his co-workers [23] have succeeded in displaying the ultrasonic field *in air* round a quartz oscillator by this method, the successive wave fronts appearing on the screen like ripples on a pond.

If it is desired to examine a progressive wave-front by direct vision it is necessary to illuminate the field stroboscopically, *i.e.*, at the same frequency as that of the ultrasonics. This can be done by passing the illuminating beam first through the quartz then back into the field. The light must be plane-polarised in a Nicol prism, crossed with the first so that no light gets through. Such will not be the case when the quartz is excited, the light stabbing period by period as the crystal vibrates. Thus the quartz may act as its own light-chopper and illuminate the field of progressive waves to which it gives rise in the fluid at the correct frequency of intermittence to make the wave-fronts appear stationary.

6. Microphones

Although small crystals of ammonium dihydrogen phosphate or of barium titanate have been used as explorers from point-to-point, and are of course best operated at resonance, microphones have also been constructed in the form of minute non-resonant condenser microphones, originally by SACERDOTE [13]. LINDSAY and his colleagues [14] have used a crystal detector of the former kind for exploring a 1.2 megacycle/sec field in water. They found that a point receiver could be constructed of such a crystal element in the shape of a cone with the apex pointing upfield. They calibrated this by applying potential to it and measuring the pressure amplitude; a typical value was $1.16 \cdot 10^{-8}$ volt per bar. With such a microphone they plotted the field of a focussing quartz crystal (*cf.* p. 9). In the same laboratory such a crystal detector mounted in a watertight housing is being used to study the scattering due to cylindrical rods in water (*vide infra*). The output from the detector is amplified, rectified and finally exhibited on a voltmeter [15].

In the propagation of ultrasonic radiation in a fluid medium, it is necessary to consider certain factors which may cause such radiation to divaricate from the simple plane-wave type. Such factors are diffraction at the source and scattering by obstacles in the medium.

7. Radiation from a Disc

At the lower ultrasonic frequencies, the wave-length in a fluid is comparable with the linear dimensions of the radiating face but at frequencies of the order of one megacycle/sec the width of the source may embrace several wave-lengths. Under the latter condition, the emission is essentially in the form of a straightforward beam, but under the former diffraction predominates. We may also distinguish between points near and far from the source.

The criterion that determines the distribution of intensity in planes parallel to the face of the emitter is the factor $m = a/\lambda$, where a is the radius of the disc. If m is large the wave front will be sensibly plane at a short distance ahead, hence the desideratum of having a source with a large superficial area. In the theory which follows, it will be assumed that the amplitude of vibration over the face of the source is uniform and co-phasal. As we have hinted earlier, uniformity of amplitude is not easy to attain; nevertheless, small surface irregularities seem to have little effect on the fluid a little way in front of the radiator. As long as the vibrations are all in phase, the fluid seems rapidly to even

References pp. 66–67

out the effect on itself of any surface irregularities of amplitude.

When m is small the effect at a distance is as of a point source, *i.e.*, the front is spherical. In deriving the equation for spherical waves, we introduce a velocity potential φ whose gradient with respect to r (distance from source) represents the particle velocity. If the velocity of the waves is c, the time derivative of this potential is related to the condensation by

$$\dot{\varphi} = -c^2 s .$$

For a diverging wave, we adopt the form

$$rs = e^{\iota k(ct-r)}, \text{ with } k = 2\pi/\lambda$$

$$\varphi = -c^2 \int s\, dt = -\frac{c}{\iota kr}(rs)$$

whence

$$\frac{\partial \varphi}{\partial r} = \frac{c}{\iota kr}\left(\frac{1}{r} + \iota k\right) rs .$$

The pressure amplitude is

$$p = -\varrho\dot{\varphi} = \frac{\varrho c^2}{r}(rs) .$$

Dividing these last expressions, we obtain the characteristic impedance of the medium to spherical radiation, as

$$z = \varrho c\left(\frac{\iota kr}{1 + \iota kr}\right) = \varrho c\left(\frac{k^2r^2 + \iota kr}{1 + k^2r^2}\right) . \tag{4}$$

The first term in this expression is a resistance but the second is a reactance and as such is frequency-dependent. If r is large, the expression reduces to ϱc as for plane waves.

If, on the other hand, we are looking at a place a short distance — compared to the wave-length — from the source, kr is small and the impedance reduces to $\varrho c k^2 r^2$, which is sometimes called the "radiation resistance" of the piston because it represents the barrier offered by the medium, in place of the ϱc that we derived earlier for a plane barrier.

We now proceed to discuss the shape of the distribution of pressure amplitude in the neighbourhood of a disc-like source of high-frequency $(m \gg 1)$ and radius a. The effect of this piston on the surroundings can be considered as made up of a set of small sources each performing vibrations $\xi_0 e^{\iota\omega t}$ distributed over its area S and radiating into a solid angle π (neglecting backward forces). The velocity potential at a distance r from the elementary source dS is then

$$d\varphi = \dot{\xi}_0 e^{\iota\omega t} \cdot \frac{e^{-\iota kr}}{2\pi r}\, dS\,.$$

and that due to the whole piston is

$$\varphi = \frac{\dot{\xi}_0 e^{\iota\omega t}}{2\pi} \iint \frac{e^{-\iota kr}}{r} \cdot dS\,.$$

Fig. 20 shows the relative intensity from the aspect of a point at a distance x along the axis, for which the potential is:

$$\frac{\dot{\xi}_0 e^{\iota\omega t}}{2\pi} \int_0^a \frac{2\pi y\, dy}{\sqrt{x^2+y^2}}\, e^{-\iota k\sqrt{x^2+y^2}} = \frac{\iota\dot{\xi}_0}{k}\, e^{\iota\omega t} \left[e^{-\iota k\sqrt{x^2+y^2}} \right]_0^a,$$

y being the radius of an annulus on the disc, distant from the point: $\sqrt{x^2+y^2} = r$.

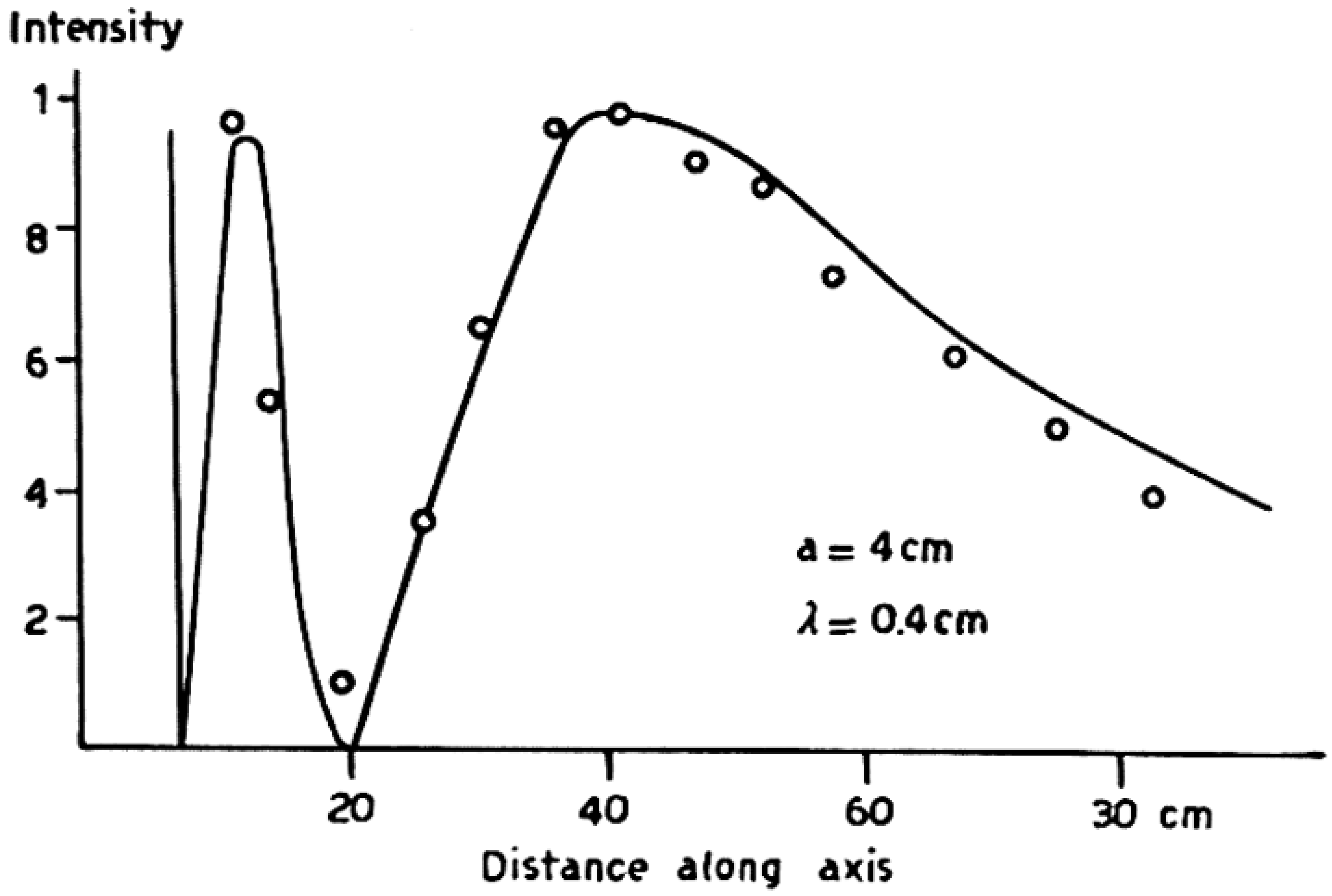

Fig. 20. Variation of Intensity along Axis of Disc Radiating into a Fluid

Introducing trigonometric functions to obtain the real part, the particle velocity at the piston becoming $\dot{\xi}_0 \cos \omega t$:

$$\varphi = -\frac{\dot{\xi}_0}{k}\left[\sin\left(\omega t - k\sqrt{x^2 + m^2\lambda^2}\right) - \sin(\omega t - kx)\right] =$$

$$= \frac{2\dot{\xi}_0}{k}\sin\left(\frac{m^2\lambda^2}{4x^2}\,k\right)\cos\left(\omega t - kx - \frac{m^2\lambda^2}{4x^2}\,k\right)$$

provided $x > m\lambda$. The pressure amplitude p is then ϱ times the maximum value of φ in the period, *i.e.*

$$p = \frac{2\varrho\dot{\xi}_0\omega}{k}\sin\left(\frac{m^2\lambda^2}{4x^2}\,k\right) = 2\varrho c\dot{\xi}_0\sin\left(\frac{\pi m^2\lambda}{2x}\right) \qquad (5)$$

Up to the point $x_0 = m^2\lambda$ along the axis, the beam is roughly parallel, but passes through a series of maxima and minima, the last occurring at x_0. From this point the beam begins to diverge at an angle which is roughly that of the angle subtended by the disc from an aspect x_0. Within this region, interference predominates as in the FRESNEL

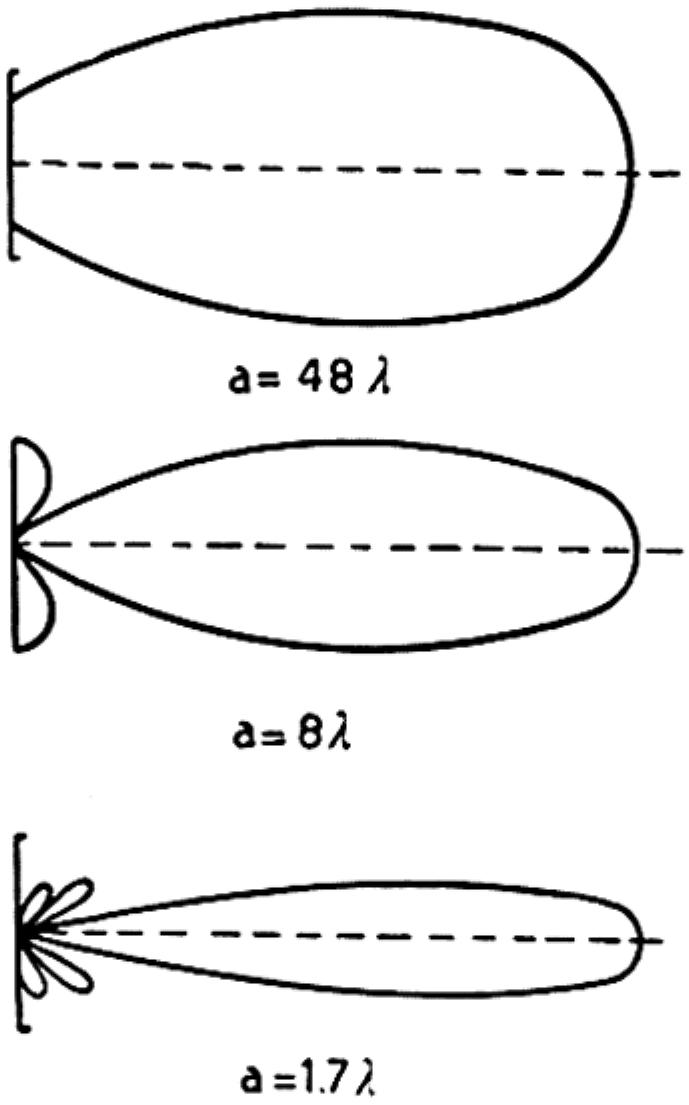

Fig. 21. Polar Curves of Radiation from Disc (Theory)

class of optical interference problems. Beyond this, the FRAUNHOFER point of view — taking parallel rays in the diffracted beam — is more appropriate, though strictly speaking we do not find close optical analogies with the

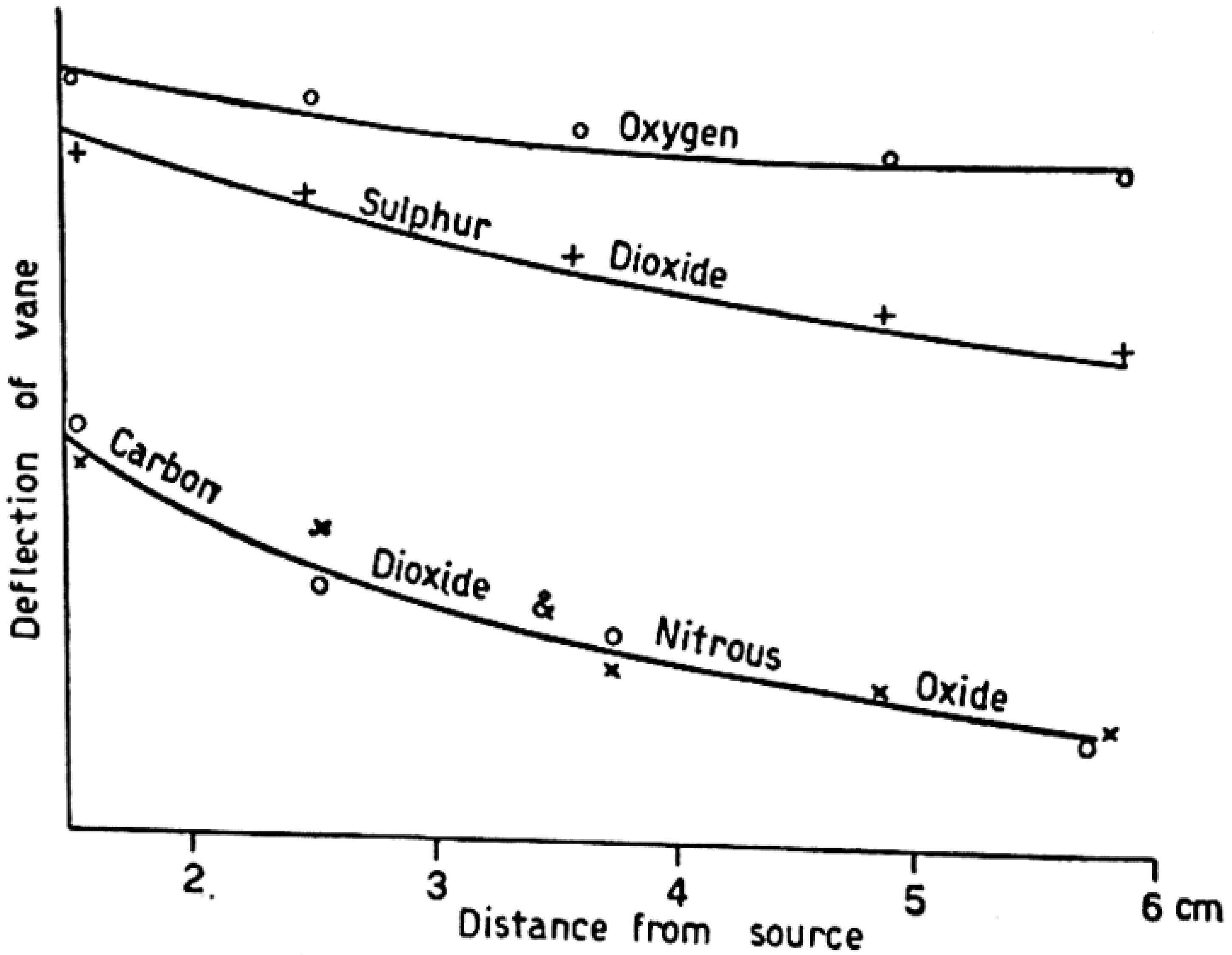

Fig. 22. Variation of Intensity with Distance from Source in Four Gases (Using Radiometer)

References pp. 66–67

experiments in ultrasonics, since we do not commonly employ ultrasonic lenses in this technique.

The next Fig. (21) shows the contours of equal amplitude [16]. In the ultimate diverging beam there are maxima and minima to be found in any cross-section perpendicular to the axis. The solid angle of the first "wing" or diffraction maxima is given theoretically by $(0.61)^2 \pi \lambda^2/a^2$.

The radiometer is not suited to precise delineation of diffraction phenomena save with large sources, since it will bestraddle a number of peaks and record an average force, but Fox and Rock have so used it in the apparatus described later (Fig. 65). This may be an advantage in certain measurements when the gross pattern of amplitude in front of the source is to be exhibited, for example, in recording absorption. Fig. 22 shows such results, taken beyond the

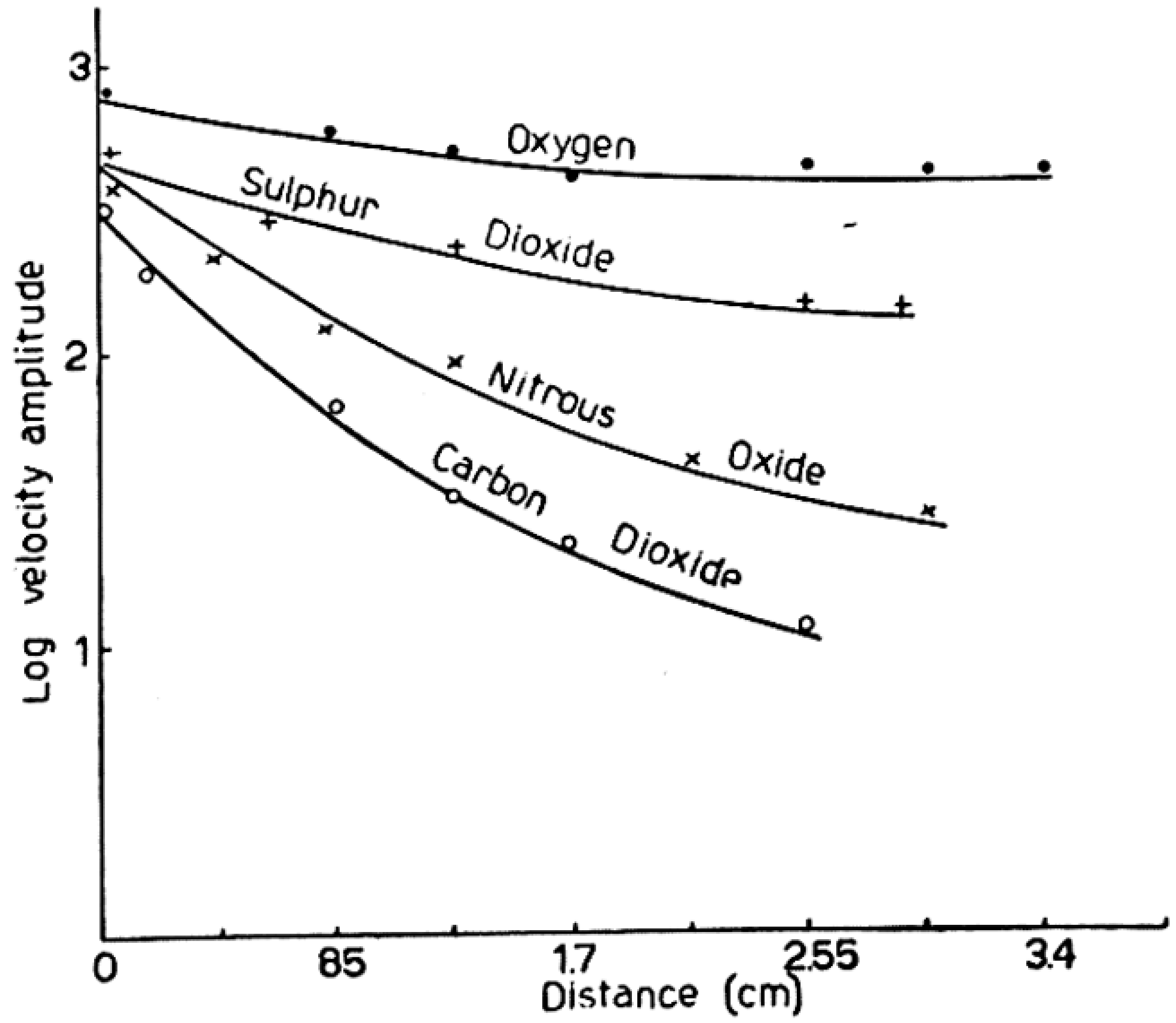

Fig. 23. Variation of Particle Velocity with Distance from Source in Four Gases (Using Hot-Wire)

Fresnel region, in four gases of different density, for a frequency of 1 megacycle/sec. The hot-wire is better suited to show the fine structure of the pattern and in the next Fig. (23) we display a set of measurements along the axis of a 695 kc/sec source plotted in logarithmic form to show that the decrease with distance beyond the last peak is only approximately exponential owing to the overlay of absorption by diffraction. Finally, in Fig. 24 appear the results of traverses perpendicular to the axis of the source

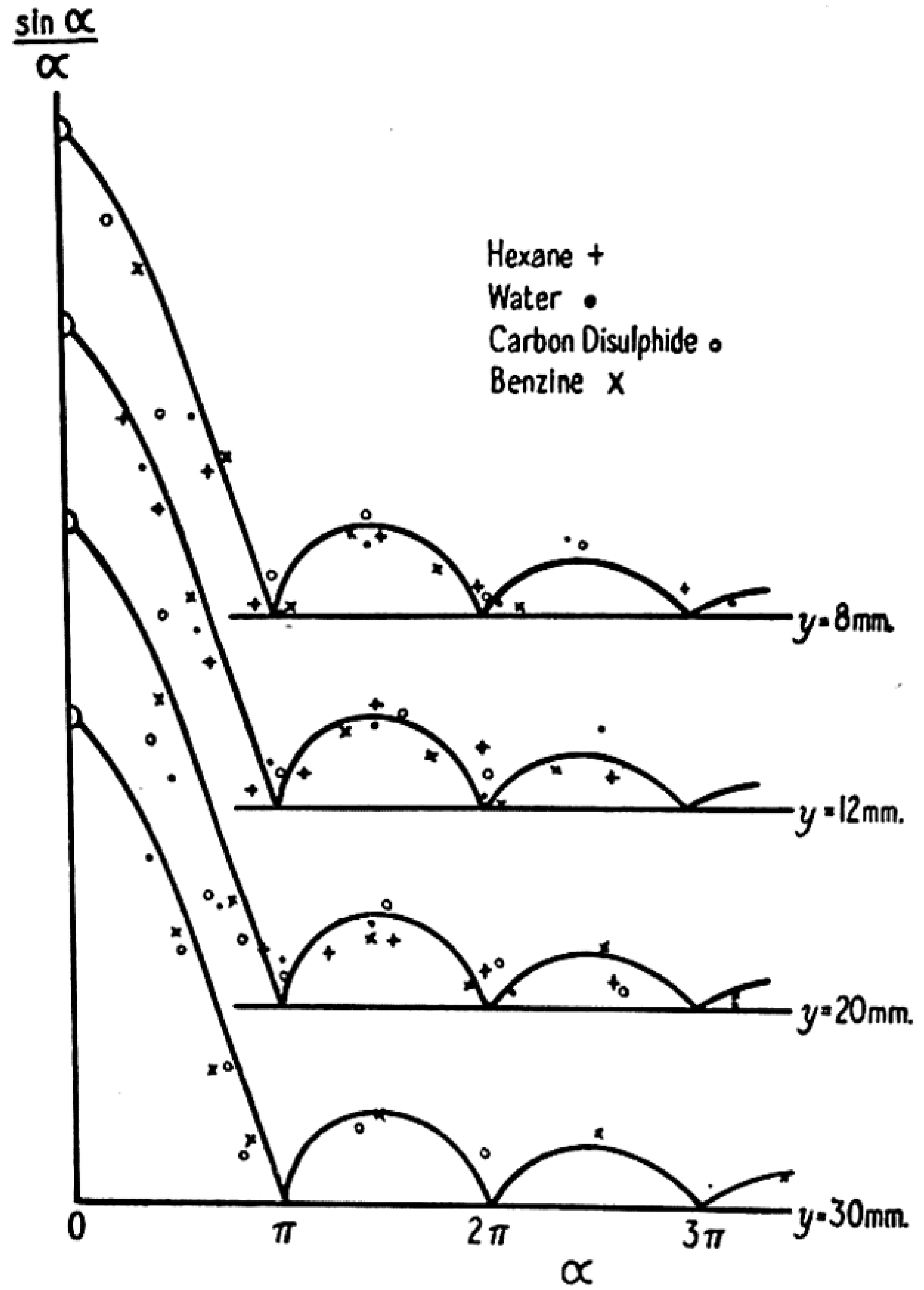

Fig. 24. Diffraction from Disc Radiating into Liquid
(y = distance of plane of traverse from source)

in liquids at 700 kc/sec, plotted as points for comparison with theory. Naturally, in such tests, it is better to let the quartz radiate through a straight slit cut as long as possible, and move the wire so that it is always parallel to the slit. It is shown in text-books on optics that the amplitude along a line parallel to the aperture of width d is $\sin \alpha/\alpha$ where $\alpha = (\pi d/\lambda) \sin \theta$, and θ is the "bearing" of the point in question. The values of the amplitude, according to this equation, are given as full lines in this figure.

It is evident that such diffraction, since it is always present more or less, will "spoil" the effects of molecular absorption such as may be taking place in the medium. In a truly plane wave (S.H.M.) such as occurs in a pipe for wave-lengths large compared to the diameter, the amplitude will be given by $\xi_0 e^{-\alpha x}$, where ξ_0 is the amplitude at the source, and α the coefficient of absorption; but with diffraction, we must make the propagation constant complex: $\alpha + i\beta$. BORN[17] has attempted to introduce such a damping factor into the equations of diffraction. Thus in place of (5) his equation for a disc of radius a is:

$$p = \frac{\dot{\xi}_0 \varrho \omega}{\sqrt{\alpha^2 + \beta^2}} \cdot \sqrt{\Big[e^{-2\alpha \sqrt{a^2 + x^2}} + e^{-2\alpha x} - } $$

$$- 2e^{-\alpha(\sqrt{a^2 + x^2} - x)} \cos \beta \left(\sqrt{a^2 + x^2} - x\right)\Big] \quad (6)$$

He shows that it is still possible to derive α from two axial measurements of pressure amplitude p_1 and p_2 provided the stations are outside the Fresnel regime. For example, at x and $x + \delta x$ the ratio

$$\frac{p_1}{p_2} = e^{\alpha x} \frac{\sin \frac{\beta}{2} \left[\sqrt{(a^2 + x^2)} - x\right]}{\sin \frac{\beta}{2} \left[\sqrt{(a^2 + \overline{x + \delta x}^2)} - \overline{x + \delta x}\right]} \tag{7a}$$

whence

$$\alpha x = \log \frac{p_1}{p_2} \cdot \frac{\sin q/(x + \delta x)}{\sin q/x}, \tag{7b}$$

if x is large compared to a and q is written for $\pi a^2/2\lambda$.

8. Reaction on Source

A medium reacts on a source pouring energy into it by virtue of the radiation resistance already evaluated as a function of z, the characteristic impedance. Explicitly, it is the ratio of this factor to the characteristic impedance of the source z_0, which counts. If we may presume plane waves, it follows from equation (2) that the ratio of the amplitude returning on itself to the original ξ/ξ_0 at the face of the emitter is $2z_0/(z_0 + z)$. As the energy in each medium is $\frac{1}{2}\varrho c\xi^2\omega^2$ the power transmission ratio — fluid to quartz — is

$$\frac{z\xi^2}{z_0\xi_0^2} = \frac{4z_0 z}{(z_0 + z)^2}. \tag{8}$$

This explains why such power may be safely transmitted from a quartz crystal into a liquid, that in air would remain "bottled up" in the quartz and perhaps fracture it. This one can appreciate by substituting the appropriate values into these expressions, *e.g.* quartz $z_0 = 125$, air $z = 0.0042$, water $z = 150{,}000$ c.g.s.

Referring back to Fig. 11 we observe that z_0 stands for the radiation resistance of the crystal and is a function of the medium and type of wave emitted. We have already noted (p. 19) that the "*Q*" of the quartz is expressed by $(\omega CR)^{-1}$, so that a measurement of *Q* when the quartz is radiating into different media will permit one to compare the characteristic impedances of such media. The *Q* may be measured by obtaining points on the resonance curve of the quartz. It may be shown that if f_1 and f_2 are two frequencies — on each side of the resonant frequency f_0 — for which the current into the crystal is $1/\sqrt{2}$ of that at resonance:

$$Q = \frac{f_0}{f_2 - f_1}\,.$$

Thus the effect of the loading of the crystal by the radiation into the medium is to increase its damping; to damp its oscillations both by lowering its response to a given applied potential at resonance and to broaden its response curve. It can be demonstrated, in fact, that the amplitude of the quartz at resonance is z_0/z times the static deformation at the same potential (BIQUARD [18]). So much for plane waves, but similar considerations apply to spherical radiation if the appropriate form of the radiation resistance is introduced into the argument [19].

VAN ITTERBEEK and DE BOCK [20] have used the delineation of the resonance curve to investigate relative impedances of liquids, exciting the quartz emitter at a tension of 2000 volts (measured on an electrostatic voltmeter). They measured the pressure of the radiation to record the intensity in the vicinity of the source. They found, as one might expect, that the form of the mounting affected the resistance; also that the sources of higher frequency showed greater damping than those of low frequency, although the expression just quoted (8) is independent of frequency. Probably, as they remark, the radiation is more truly plane at the higher frequencies. Owing to the naturally strong resonance (high Q) ,the resonance curves are not easy to delineate, even under loading.

9. Change of Wave-Form

Associated with high intensity of the source, the wave may have a wave-form in the immediate vicinity which is not sinusoidal, *i.e.*, it may contain overtones. A sine-wave of large amplitude tends towards one of saw-tooth type gradually as it progresses. This *déferlement*, as BIQUARD calls it, was originally discussed by RAYLEIGH [21] and later by FAY [22], who showed that, owing to differences in absorption and propagation between the Fourier components that make up the steep-fronted wave, the discontinuity becomes smoothed out and the type eventually reverts to sinusoidal.

Changes in the wave-form of this nature have been detected in spark photographs of the wave system in front of a quartz emitter by HUBBARD[23] and his colleagues. They submit such a photograph to microphotometry and can observe the change in wave-form. BIQUARD[18] calculated, in connection with his measurements of absorption in liquids, the amplitude of the fluid motion in front of the quartz (*cf.* p. 162), and so, the distance required for the discontinuity to be established.

In most cases, it was greater than the distance over which the measurements were made, but was within the distance (10 cm) over which his results in ether were obtained. He points out the necessity for a check of this nature, since the mean absorption of the saw-toothed wave is much greater than of the sinusoidal type.

10. "Streaming" from an Acoustic Source

A source of trouble in all attempts to make measurements in the medium near a source, such as a vibrating quartz, in a tube is the "streaming" away from the source, with return along the walls in the form of circulations like stationary vortices which are set up in this neighbourhood. Fig. 25 is a drawing based on a photograph of LIEBER-

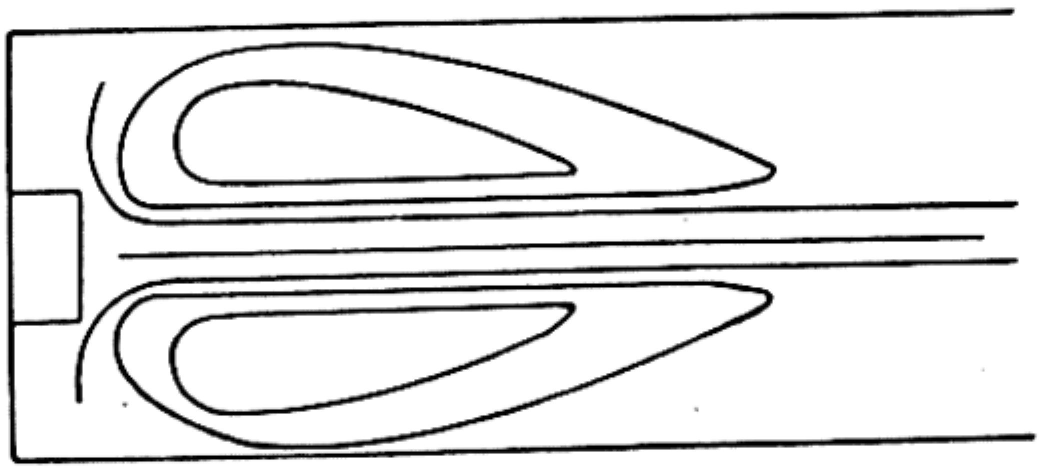

Fig. 25. Circulations in Front of Quartz Emitter (LIEBERMANN)

MANN [24] in a liquid containing aluminium particles in suspension, showing the circulations in front of a quartz emitter at one end of a tube.

ECKART [25] explains these on the basis of a second approximation to the hydrodynamical equations of STOKES, whereby the possibility of a liquid having compressional viscosity as well as shear viscosity must be envisaged (*cf.* p. 286).

Actually, however, the same phenomenon may be demonstrated in a *gas*, which is not usually supposed to possess anything but ordinary viscosity. The experiment indeed, has a respectable antiquity, since it stems from observations of the circulations in Kundt's tube. It is indeed, possible to reverse the roles of source and fluid in this experiment. Some years ago ANDRADE [2] placed a ball-bearing in the centre of a column of air in which smoke particles were in suspension and observed, when sound waves were led into the containing tube, streaming rotations which circumscribed the obstacle in four quadrantal vortices.

The shape of these was calculated by SCHLICHTING [26] using the "boundary layer" theory in which the viscosity of the fluid is neglected save in close proximity to the solid walls and face of the obstacle. The analysis shows that a stationary streaming is set up, whose value at any distance x is $\frac{\dot{\xi}}{\omega} \cdot \frac{\partial \dot{\xi}}{\partial x}$. The fluid moves toward that part of the field where the amplitude of the oscillatory motion (parallel to the wall) is least. In the case we have cited, of a cylinder of radius a and velocity amplitude $\dot{\xi}_0$ sending longitudinal waves into the fluid, the "streaming velocity" in line of the vibration (axis of the tube) is proportional to $\dot{\xi}_0^2/a\omega$. ECKART, on the basis of his theory, would make the streaming velocity proportional to ω^2/c^4. Herein lies a possibility of testing the two theories.

Since the effect depends on $\dot{\xi}_0^2$ it behoves the experimenter to keep the amplitude of his source small if he wants to avoid this "quartz wind" as it is also called.

11. Cavitation

Another phenomenon which may upset one's measurements in a liquid medium (only), if high amplitude is tolerated in the source, is the formation of vacuous cavities.

True cavitation occurs whenever the pressure on the parts of a body rapidly moving in a liquid in which it is immersed is reduced so low by the incapability of the flow to follow the surface that a vacuum is produced, or at anyrate, a region saturated only with the vapour of the liquid.

If locally the pressure is reduced to the vapour pressure, cavitation ensues. In unsteady motion such as we have in ultrasonics, cavities may form without much change in the mean velocity U or pressure p. Thus diaphragms having large accelerations and hence pressure reductions on their surfaces will cavitate readily and this the more so if the general hydrostatic pressure p is nearly atmospheric. If there are any dissolved gases, these will come out and evaporate into the cavities which they will encourage to form just as in boiling a liquid containing dissolved air. If then it is desired to inhibit ultrasonic cavitation in liquids we have four remedies at our disposal; (1) use low power, (2) use high hydrostatic pressure, (3) use a liquid with small vapour pressure, (4) make sure that all dissolved gas has been removed.

In hydrodynamics, it is usual to define a "cavitation number" $\zeta = (p - p_0)/\frac{1}{2}\varrho U^2$ such that cavitation is likely to set in at a specified value of ζ in a given fluid regime. In our study it seems better to employ in the denominator in place of $\frac{1}{2}\varrho U^2$ the pressure amplitude in the radiation which is $\varrho c \xi \omega$, writing then $\zeta = (p - p_0)/\varrho c \bar{\xi} \omega$. It seems that ultrasonic cavitation may appear at much higher values of ζ —, *i.e.*, more readily — than ordinary cavitation in straightforward fluid motion, though it is also true that in the latter case one rarely measures the local velocity at the place where the cavity is born and this may be considerably different from the mean stream speed.

When the power applied to a transducer is increased to the point at which cavitation sets in, bubbles are seen in the liquid and an audible noise, apparently due to the collapse of the bubbles, is produced. The cavities often form at a nucleus near the transducer surface, with a "meteor tail" spreading away from the "head". These may persist for the duration of the signal from the source.

Many of the special actions of power ultrasonics such as coagulation, disruption, and chemical reactions in liquids, which have been discovered, are ascribed to the formation, and more particularly, the collapse of such cavities. In the latter process very high accelerations can achieve actions between particles in the liquid not readily attainable by other means [27].

12. Scattering of Ultrasonics by Obstacles

This is an important aspect of the propagation of ultrasonics in relation to the smokes, suspensions and the possibilities of molecular scattering. We have already remarked (p. 33) on the mobility which a solid or liquid particle in suspension in a gas exhibits in a greater or lesser degree when placed in the field. It is the mobility, or rather immobility, which determines the amplitude in the scattered radiation. If an object is completely mobile in a group of plane waves which pass over it, like a small piece of paper on a pond, it contributes nothing to the wave system, which has the same shape behind it as before. If, on the other hand, it is fixed like a post partly submerged in the pond, it acts as a source of waves, sending them out in nearly spherical form, and these have to be added to the original plane waves to get the complete system, applying the boundary condition that the outward particle velocity must be zero at the surface of the obstacle. It can be shown that the emitted radiation is the same as that of a double source — corresponding to a dipole in electro-magnetism — at the centre of the obstacle, assumed symmetrical, *i.e.*, a circular cylinder or sphere.

Let the double source have an equation of motion:

$$m\ddot{\xi} + m/\tau \cdot \dot{\xi} + m\omega_0^2\,\xi = Fe^{\iota\omega t} \tag{9}$$

where ω_0 is its natural pulsatance, defined as 2π times that frequency which it would have if displaced and let go without damping. τ is a time of relaxation of the source, and the term on the right-hand side represents the forcing owing to its reaction to the oncoming waves.

The amplitude of response of this source will then be:

$$A = \frac{F/m}{(\omega_0^2 - \omega^2) + \iota\omega/\tau}\,. \tag{10}$$

This source will then emit and the resulting field may appear quite complicated when analysed on a point-to-point basis, often Often however, we are more interested in the rate of emission energy by the scatterer. Since the mean value of the energy in S.H.M. is $\omega^2 A^2$, we obtain, after seeking the real part of the last expression, the scattering coefficient of the obstacle as

$$\sigma = \frac{\omega^2\,F^2/m^2}{\sqrt{(\omega_0^2 - \omega^2)^2 + (\omega/\tau)^2}}\,, \tag{11}$$

in which an undetermined "form factor" for the shape of the obstacle has been omitted. But the amplitude at a distance must depend on the scattering volume (in virtue of the way that the obstacle scatters, on this theory) and so, inversely as the distance, in order that we may introduce another non-dimensional factor. This done, we may consider three cases.

1. ω small compared to ω_0. Then:

$$\sigma = \frac{F^2}{m^2}\left(\frac{\omega}{\omega_0}\right)^2 .$$

The scattered amplitude is proportional to ω^2 or to λ^{-2}. Since this expression was first derived by RAYLEIGH to explain the scattering of light by small particles, it is known as RAYLEIGH scattering. It will occur less frequently in ultrasonics, where λ is already small compared to likely obstacles, unless they are microscopic (*cf.* p. 270).

2. ω large compared to ω_0. Then σ is independent of λ:

$$\sigma = F^2/m^2 .$$

This case, which occurs when ultrasonics strike a large obstacle, corresponds to the "specular reflection" of a mirror.

3. ω near to ω_0 in value. Here a form of resonance occurs, the scattering being very large for $\omega \equiv \omega_0$. In this case too, the velocity of propagation is affected, if the incident rays pass through an assemblage of scattering bodies all having the same natural frequency. This corresponds to "anomalous dispersion" in light, so that the refractive index (to ultrasonics or light) of the resonant assembly changes rapidly with oncoming frequency. We shall refer later to experiments which demonstrate this.

A general question poses itself when there are present a number of obstacles in place of the one which the theory pictures, *i.e.*, what happens to the scattered energy when it subsequently encounters another obstacle? This is very difficult to answer precisely, but it is obvious that in a crowded assembly further scattering must ensue, and in the limit the sound energy will be diffused instead of being propagated by waves as we understand them. Again, this means that phase relationships are lost and the radiation becomes incoherent, somewhat in the fashion that white light is described as incoherent. (Something like this occurs, without the intervention of visible obstacles, when sound waves traverse a very turbulent atmosphere). In general, the total amount of scattered energy will then depend on the population of objects per unit volume, (*cf.* p. 274).

There is another aspect of resonant scattering which our outline of the theory does not touch. Suppose there is a regular pattern of scattering bodies, *e.g.*, a line of equi-spaced spheres or a lattice in three dimensions of such spheres. On the face of it, such a system will act as a grating and scatter or, rather, diffract light regularly in specified directions. The velocity will also pass through the variations characteristic of anomalous dispersion (as in the corresponding optical problem) in the neighbourhood of resonance (*cf.* Fig. 26) as BELIKOV [28] has shown when an audible sound wave passed through a system of Helmholtz resonators mounted in a chamber. The author has found the same effect when ultrasonic waves pass through a lattice made of equi-spaced wires in an air interferometer.

As the temperature is changed so that the ultrasonic wave-length passes through a series of values in the vicinity of double the spacing of the wires the velocity as measured on the interferometer passes through a change like that of Fig. 26 and there is marked attenuation. This kind of resonant scattering, which we may not often find with solids in suspension in a gas, owing to the badly matched impedance, can occur in an emulsion of two liquids which do not mix or of regular-sized crystals which form under the action of ultrasonics in a metal melt as it is solidifying (*vide* Chap. VIII).

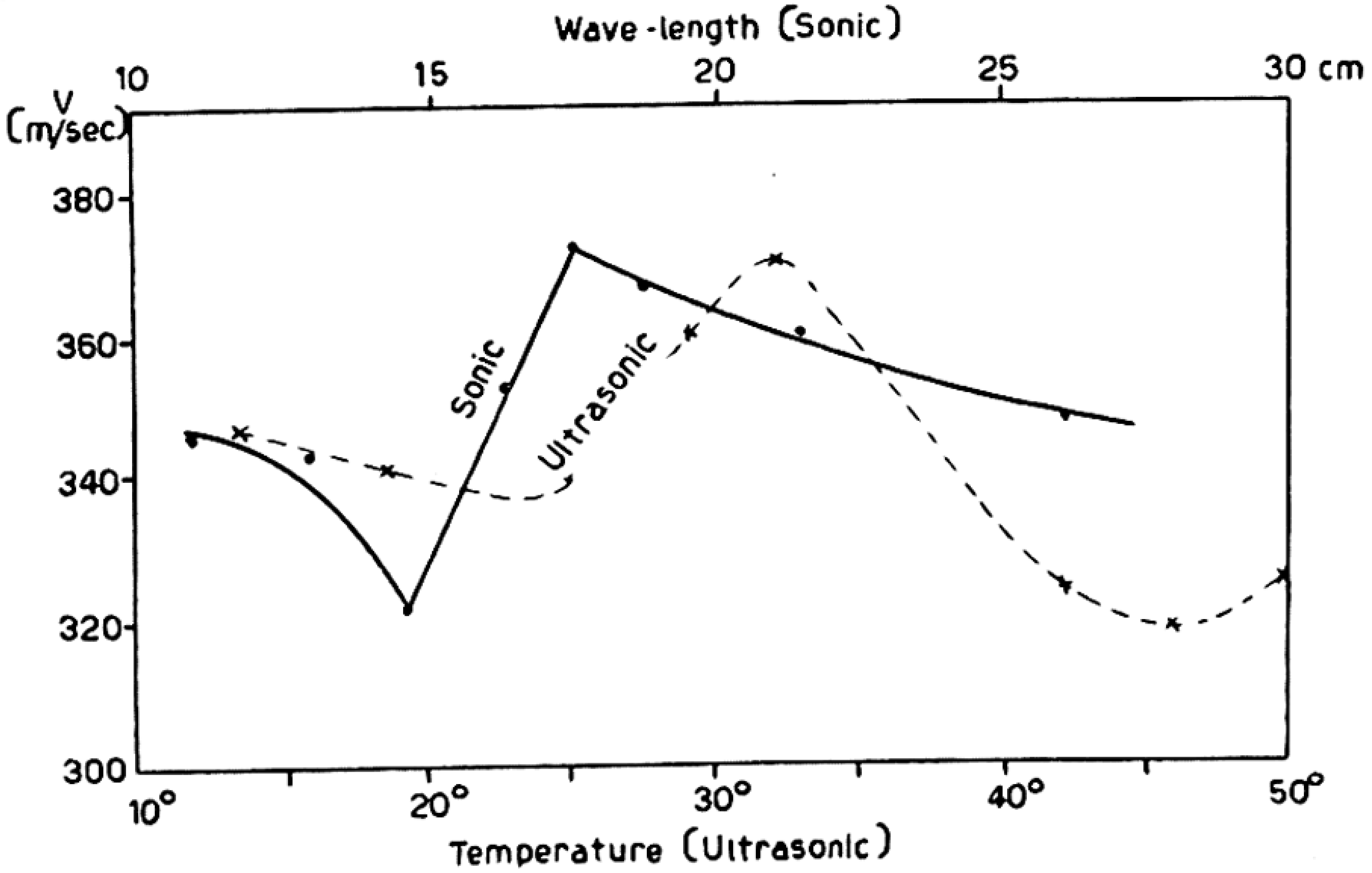

Fig. 26. Anomalous Dispersion of Sound and Ultrasonics (BELIKOV; RICHARDSON)

LINDSAY and his associates have studied the scattering of an ultrasonic beam under water when it strikes an obstacle of size not much wider than the wave-length, in the form both of a solid cylinder and a hollow cylinder enclosing liquid (TAMARKIN [29]). The enclosed liquids provided a range of values of acoustic impedance. Traverses of pressure amplitude in planes behind the obstacle gave comparable data for scattering theory. The scattering proved to lie in the transition region between the RAYLEIGH and specular types of field distortion, wherein diffraction is more noticeable than diffusion. Scattering still takes place if the two liquids (within and outside) the cylinder are matched in impedance provided there is a difference of acoustic velocity.

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CHAPTER III

MEASUREMENT OF PROPAGATION CONSTANTS

The most accurate methods of measuring the propagation constants, *i.e.*, the velocity and absorption, of ultrasonics in fluids are based on the setting-up of resonances by stationary waves — reputed plane — in a column limited by the source at one end and a plane reflector at the other. For liquids there is also available the ultrasonic diffraction grating which is very accurate for wave-length but less satisfactory where absorption is in question.

1. The Pierce Interferometer

In the original interferometer of PIERCE[1], the movement of the reflector as it passed through resonant and anti-resonant positions caused a reaction on the quartz crystal source whereby the grid voltage and — with it — the plate current varied. Fig. 27a shows a simple form of the Pierce circuit while 27b gives a more elaborate type in which beside the milliammeter A, a galvanometer G with variable shunt R_2 is available to measure the anode current. Further,

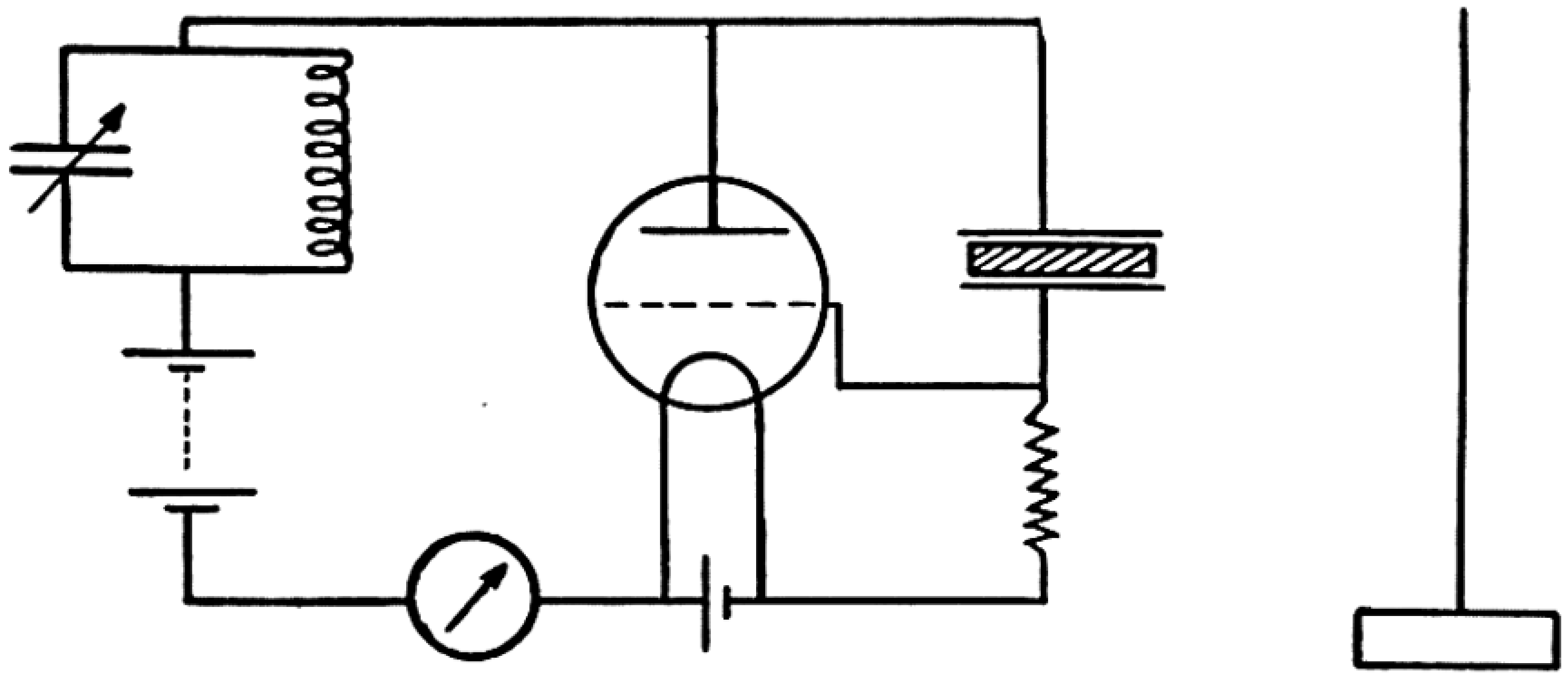

Fig. 27a. Simple Pierce Interferometer

by switching in the voltaic cell *B* and its associated resistances *P* and R_1, *G* may be "backed-off" to record small current changes caused by movement of the reflector.

When the waves returning from the reflector reach the source in opposition of phase, they not only change the amplitude of the oscillations but shift the mean value of the anode current. It is this shift in the mean which one observes on the galvanometer as a crevasse in the anode

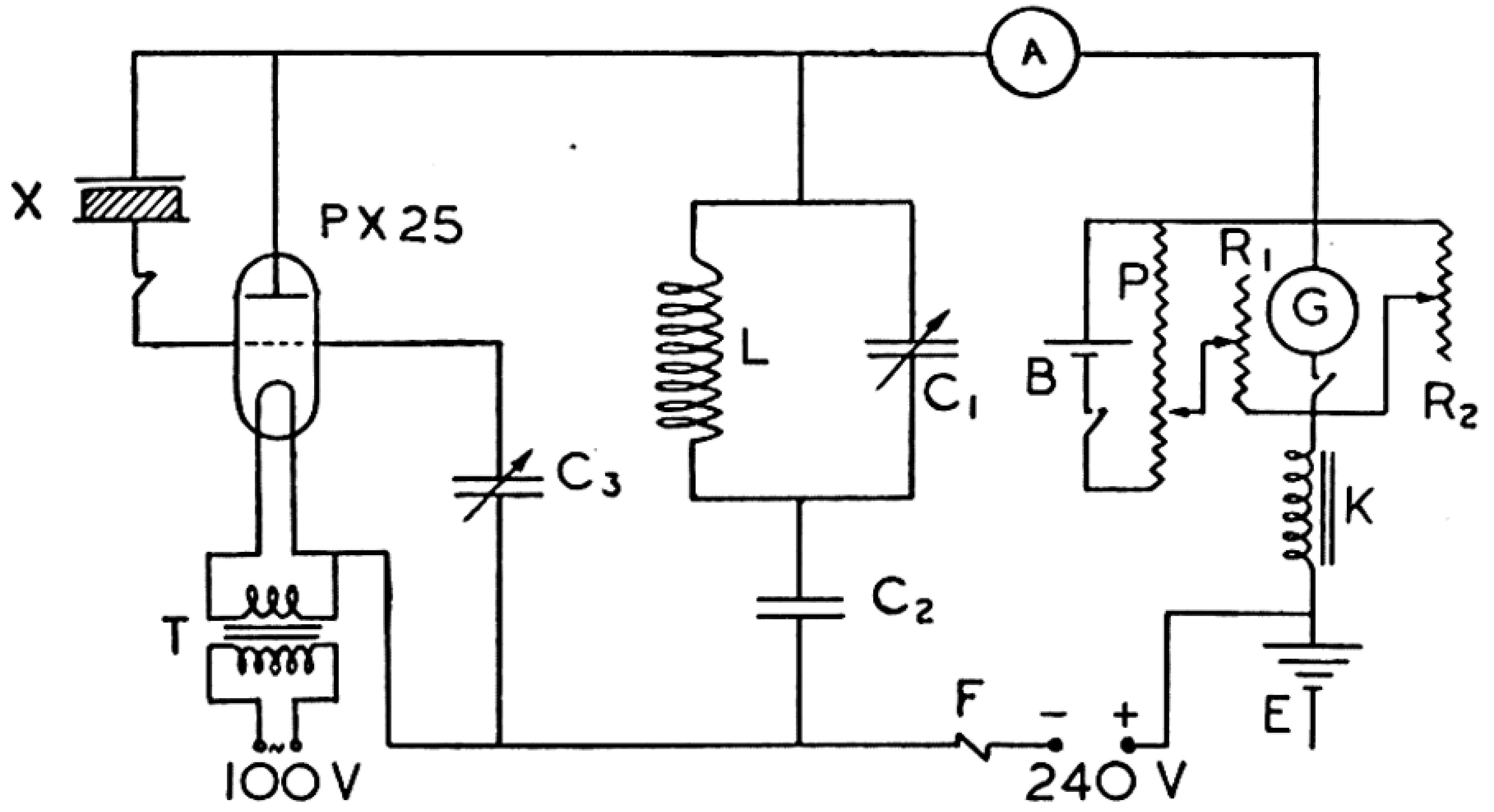

Fig. 27b. Power Circuit for Driving Crystal with Reaction Detector

current, occurring once every half wave-length of the reflector's motion.

Fig. 28 shows, by the two curved lines, the trend of the maxima and minima of anode current, as the reflector is moved away from the source in a medium in which attenuation of the intensity on the wave-front — whether by diffraction or true absorption — is taking place. The peaks rest on the upper curve, the crevasses on the lower, the undisturbed value — in the absence of reaction — being indicated by the horizontal line. It will be noted that after two or three peaks; the reactions settle down to a steady diminution with distance, from which the attenuation coefficient can be calculated (p. 74).

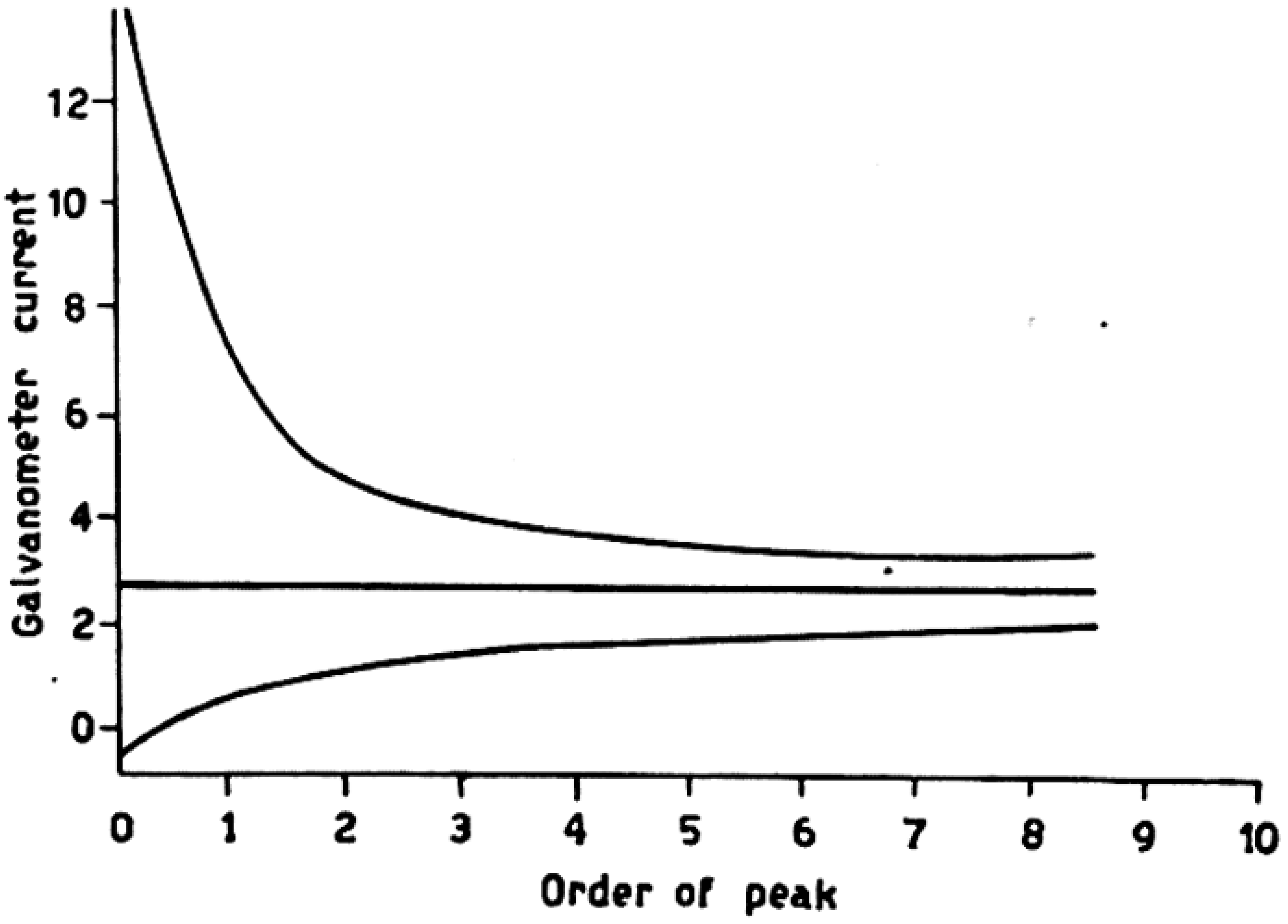

Fig. 28. Loci of Maxima and Minima in Reaction as Reflector is Moved (KRASNOOSHKIN)

If the frequency of the quartz is measured at the same time by loose coupling of the driving circuit at *K* to a "wave meter", the velocity of the waves in the fluid can be determined. (There is a slight change of frequency with fluid load, *i.e.* with length of column.) From the size of the crevasses, the absorption coefficient in the fluid as the reflector is withdrawn can be calculated. This is a more intricate problem, since — apart from the possibility of the waves diverging as they progress, a matter we discussed in the last chapter — it involves considerations of the *magnitude* of the reactions in the circuit in relation to the amplitude of the retrogressive waves.

2. The Fixed-Path Interferometer

Before tackling this, we shall consider a later type of resonant column in which the system of stationary waves set up by the nature and position of the reflector remains fixed in extent while a suitable probe explores the interspace. The probe is usually a small hot-wire (*cf.* p. 41) which offers negligible obstruction to the column being probed[2]. The equation to such a "fixed path interferometer" may be derived as follows, supposing in the first instance that the waves are truly plane and perfectly reflected at the far end of the column. Let us suppose the progressive and retrogressive waves of a dispersive gas are given by the expression

$$\dot{\xi}_1 = B\,\mathrm{e}^{-\alpha x}\,\mathrm{e}^{\iota(\omega t - \beta x)}\,; \qquad \dot{\xi}_2 = C\,\mathrm{e}^{\alpha x}\,\mathrm{e}^{\iota(\omega t + \beta x)}\,. \qquad (12)$$

Since $\dot{\xi} = 0$ at $x = l$, *viz.* at the reflector,

$$0 = B\,\mathrm{e}^{-(\alpha + \iota\beta)l} + C\,\mathrm{e}^{(\alpha + \iota\beta)l}\,.$$

Therefore

$$\dot{\xi} = C\,\mathrm{e}^{(\alpha + \iota\beta)l}\left[\mathrm{e}^{(\alpha + \iota\beta)(x - l)} - \mathrm{e}^{-(\alpha + \iota\beta)(x - l)}\right]\mathrm{e}^{\iota\omega t}$$

$$= 2C\,\mathrm{e}^{(\alpha + \iota\beta)l}\sinh\left\{(\alpha + \iota\beta)(x - l)\right\}\mathrm{e}^{\iota\omega t}\,.$$

Whence (putting $A = C\mathrm{e}^{\alpha l}$ and omitting the time factor)

$$\overline{\dot{\xi}^2} = 2A^2\left[\cosh\left\{2\alpha(x - l)\right\} - \cos\left\{2\beta(x - l)\right\}\right]. \quad (13)$$

As α is usually small compared to β, the maximum and minimum values of $\bar{\dot{\xi}}$ as x varies are given by $2A\cosh\{\alpha(x - l)\}$ and $2A\sinh\{\alpha(x - l)\}$, so that by tracing out the peaks and troughs in the pseudo-stationary waves, both α and β can be determined. Note that it is also permissible to vary l while the site x of hot-wire is kept fixed. With the same approximation, the peaks and troughs in the readings of $\bar{\dot{\xi}}$ are to be obtained by substitution in the expressions just quoted to get the two propagation constants, but in this case $\mathrm{e}^{\alpha l}$, which represents the amplitude of the waves at the source, varies with l. This alters the reaction on the crystal and so needs the consideration of the "variable path interferometer", which follows shortly.

The above theory suffices for the fixed path interferometer in a gas, where the impedance of the medium is so small compared to that of the solid source and reflector that their impedances may be considered as infinite. (But there may be some exceptions to this at high frequencies, *vide infra* p. 78). In a liquid however, with its higher characteristic impedance, the reflector and the medium may be more nearly matched in impedance and we must no longer take the amplitude on reflection to be equal to that in the oncoming wave, nor the reversal of phase to be complete. The corresponding expressions to (12a) and (12b) are now:

$$\dot{\xi}_1 = \frac{e^{-(\alpha + \iota\beta)x}}{1 - \gamma\, e^{-(\alpha + \iota\beta)2l}}\, e^{\iota\omega t} \qquad (14a)$$

$$\dot{\xi}_2 = \frac{1 - \gamma\, e^{-(\alpha + \iota\beta)(2l - x)}}{1 - \gamma\, e^{-(\alpha + \iota\beta)2l}}\, e^{\iota\omega t} \qquad (14b)$$

where γ is the amplitude reflection coefficient at the solid boundary. The amplitude at the reflector is then

$$\frac{(2 - \gamma)\, e^{-(\alpha + \iota\beta)l}}{1 - \gamma\, e^{-(\alpha + \iota\beta)2l}}$$

which can be represented as $e^{\iota\delta}$ where δ is a phase shift in the reflected waves due to the solid terminals transmitting energy. Then it is possible to rewrite the equations (12) to (13) adding the constant phase shift δ in the exponentials and, so, in the hyperbolic functions eqn. (12). This angle should also be introduced at both ends of the column, not necessarily in the same degree, though to avoid complications we shall assume that the terminal impedances are the same, as though the reflector were likewise made of quartz — as indeed it may be in the transmitter-receiver type of interferometer (see p. 77).

3. The Variable-Path Interferometer

The pressure at the source is found by multiplying the particle velocity there by the characteristic impedance of the medium and a factor dependent on the impedance of the column, derived from the equations already given. This factor is the particle velocity at the point and, following HUBBARD [3], we can divide it into two parts, one dependent and one independent of frequency, thus:

$$p_0 = \varrho c \dot{\xi}_0 (P + \omega Q) .$$

The factors turning out to be:

$$P = \frac{\sinh (2al + \delta)}{\cosh (2al + \delta) - \cos 2\beta l};$$

$$Q = \frac{\sin 2\beta l}{\cosh (2al + \delta) - \cos 2\beta l}.$$

At a resonance, where βl is zero, we find

$$p_{\max} = \varrho c \dot{\xi}_0 \frac{\sinh (2al + \delta)}{\cosh (2al + \delta) - 1} . \tag{15a}$$

The minimum value of p occurs for a further increase of length of $\lambda/4$ to l' and is:

$$p_{\min} = \varrho c \dot{\xi}_0 \frac{\sinh (2al' + \delta)}{\cosh (2al' + \delta) - 1} . \tag{15b}$$

The difference of these values may be read off from the circuit to give us the value of a.

HUBBARD [3] and others [4] couple the quartz oscillator to a constant-frequency valve oscillator which incorporates a vacuum thermo-couple recording on a sensitive galvanometer. An e.m.f. $E_0 e^{\iota\omega t}$ is induced in the thermo-couple (of resistance R_1) giving rise to a current of amplitude $I_0 = E_0/R_1$ when the interferometer is disconnected. When the interferometer is in circuit the current is i_0. The quantity $\sigma^2 = i_0^2/I_0^2$ as a function of l the path-length, is obtained from the experiment. The velocity of the ultrasonic waves is then derived from the periodicity in σ.

Fox [5] applied this method to liquids. He showed that

$$\sigma^2 = \frac{(1 + SP)^2 + (SQ)^2}{(1 + SP + C)^2 + (SQ)^2}, \qquad (16)$$

where $S = Ae\varrho c$; $C^{-1} = \omega Ri\,(C_1 + C)$; $i = \omega R_1\,(C_1 + C)$. Here R and C are the equivalent resistance and capacitance of the quartz at resonance (Fig. 11), C_1 the capacitance of the pick-up circuit: i the thermoelectric current, A the effective-area of the quartz in contact with the liquid: e the piezo-electric constant of the quartz.

The fluid column introduces modifications of R and C^{-1} into $R + SP$ and $C^{-1} + \omega SQ$, where P and Q are functions of α, γ, x and l.

In a liquid P and Q are small, but not so small as in a gas, where they are practically zero. In all gases σ keeps

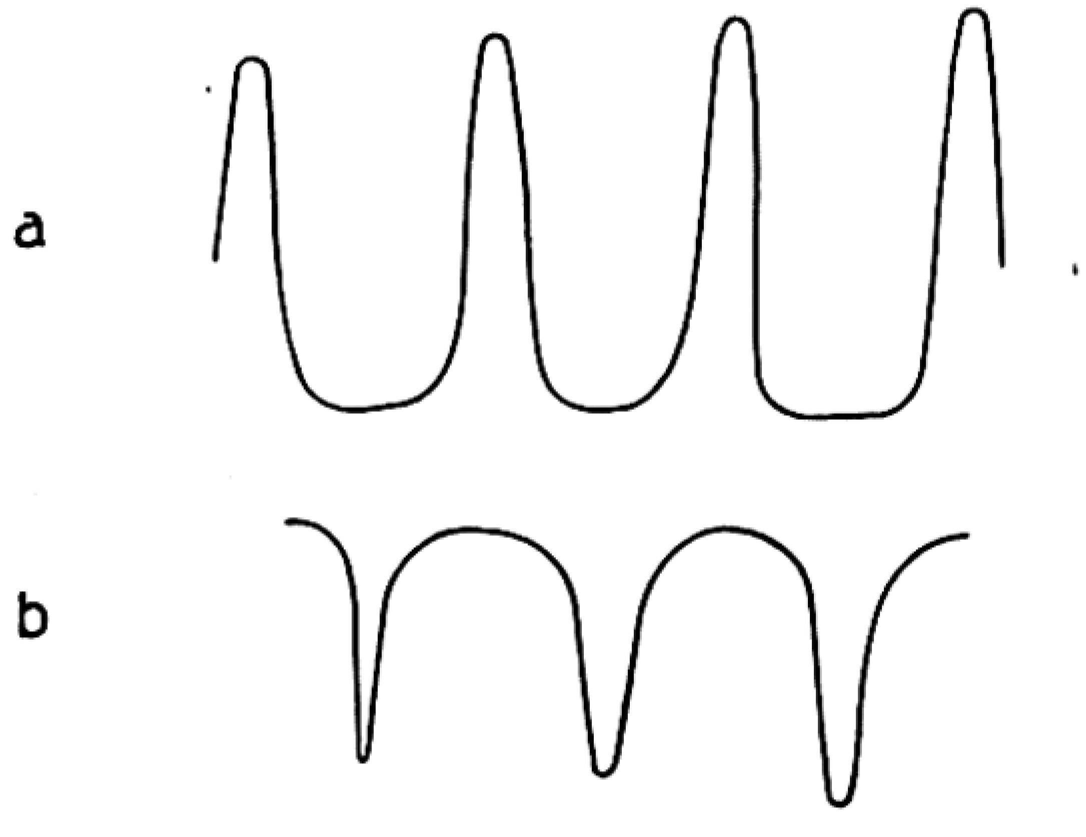

Fig. 29. Peaks in Anode Current (a) in a Gas, (b) in a Liquid

close to unity except at multiples of l equal to $\lambda/2$, when there is a sharp rise and fall, but in liquids the changes in σ resulting from the larger changes in P and Q (eqn. 16) as the column lengthens occur at $(2n+1)\lambda/4$ positions. Also the peak in the gas is inverted into a crevasse (in σ) in the liquid. Fig. 29 shows typical peaks in a gas ($\gamma \approx 1$) and in a liquid ($\gamma = 0.8$). Fox [5] points out that the characteristic impedance (ϱc) of a gas is of order 40, of a liquid of order 10^4, while that of a metal (reflector) is $5 \cdot 10^6$. It is the large reflection coefficient that thereby results and the small absorption in the liquid that makes it necessary to modify the interferometer theory. It keeps SP and SQ large and σ close to unity except at the $(2n+1)\lambda/4$ locations where $Q = 0$ and P is a minimum. The depth and width of the resulting crevasse in σ depends on the constants of the composite system: quartz plus fluid plus reflector.

HARDY [6] has pointed out that if the reflector is used in a region so far from the source that $\lambda/4$ is a small fraction of l, the difference between the two values of p given in eqn. (15), allows of a simplification to

$$\Delta p = \frac{2\varrho c \dot{\xi}_0}{\sinh(2al + \delta)} \cdot \tag{17}$$

(A discarded term involves $a^2\lambda^2$ as coefficient. The latter quantity is negligible in practical ultrasonics.)

The reaction on the driving circuit causes a proportionate change in grid voltage as the path is lengthened. This again results in a proportionate change in mean anode current, the quantity that is measured. When l is large, we can in fact consider the resistance of the source to be constant. Thus if ΔI_A, ΔI_B, ΔE_A, ΔE_B are the differences between the respective values of these quantities at resonance and anti-resonance respectively, for two distances l_A and l_B:

$$\frac{\Delta I_A}{\Delta I_B} = \frac{\Delta E_A}{\Delta E_B} = \frac{\Delta p_A}{\Delta p_B} = \frac{\sinh 2\alpha l_B}{\sinh 2\alpha l_A},$$

or

$$\log_e (\Delta I_A/\Delta I_B) = 2\alpha (l_B - l_A)\,. \tag{18}$$

This suggests a simple way of getting rid of the unknown δ and of deriving α from a series of resonant and anti-resonant peaks in the anode current as the reflector is moved. Correction may of course still be needed for diffraction effects.

FRY[7] has discussed the theory of the double quartz interferometer which has occasionally been used for gases: that in which the two crystals, matched as to frequency, face each other across an intervening fluid space. One of them is excited at an r.m.s. voltage E_1 and the problem is to calculate the impedance of the gas column of specified length from a knowledge of the voltage E_2 generated in the second. If, as the latter is moved, the envelopes of the maxima and minima in E_1/E_2 are plotted against l, the resulting curves are found to follow a hyperbolic sine and cosine respectively of αl.

4. Thermal Absorption

This point is opportune to refer to a form of absorption that may occur at fluid-solid interfaces due to the transmission of thermal waves, first suggested on theoretical grounds by HERZFELD[8]. In fact, the pressure on the reflector gives rise not only to a reflected compressional wave but also to thermal waves — such as those we shall discuss in Chapter VII in another connection — one set passing into the solid and another back into the fluid in order to maintain the boundary conditions at the interface. These waves are rapidly damped but, because, in the gas they are out of phase with the ordinary wave, they reduce its amplitude. In mixed radiation, thermal waves have propagation constants dependent on frequency (*cf.* p. 203) which means that the coefficient, such as δ in the equations (15), (17) above, is complex. In practice, the frequency of the waves in an acoustic interferometer is single-valued, so that, if we wish to introduce this effect we can do so as an accession to that value of δ appropriate to the mis-match of impedance at the boundary. Actually the factor requires to vary as $\sqrt{f}$. In a gas interferometer at high ultrasonic frequency this thermal effect can quite swamp the effect of mis-matched impedance. In a liquid, especially at low frequencies, the impedance reflection is more important.

5. Satellites: Effects of Radial Waves

Early in the practice of interferometry, subsidiary peaks or crevasses were sometimes observed between or sometimes overlaying the main peaks and having no apparent cyclic relation to them. These have been ascribed by some authors to energy in the diffraction wings (p. 50) which has found its way by a longer route than the main beam back to the source, either by reflection from the walls of the container or from the reflector itself when this was slightly inclined to the main wave-front. Nevertheless, in certain interfero-

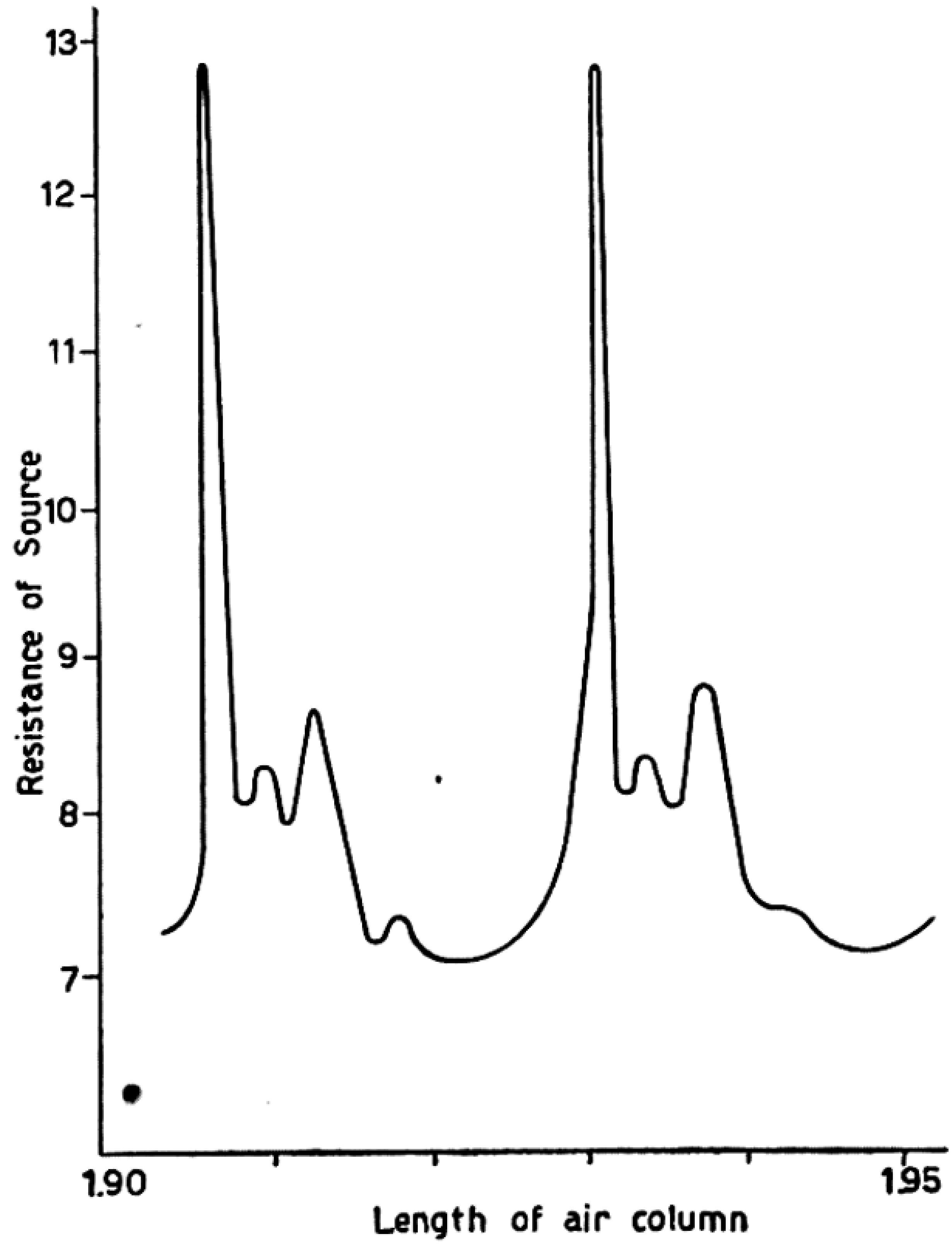

Fig. 30. Satellites in a Gas (BELL)

meters these "satellites" have persisted even after all care has been taken in aligning the reflector parallel to the face of the source; perhaps, by making an optical interferometer of the interspace and assuring the accuracy by observing (optical) interference fringes. One such careful adjustment left the satellites shown in Fig. 30, some quite distinct from the principal summits, others attached to the two main peaks, with a "col" between. The satellites often have a periodicity of their own, though this is unrelated to that of the waves passing along the axis which are the subjects of study. JATKAR [9] first hinted at their origin as radial waves having wave-lengths determined by the *width* of the cylindrical tube which often forms the container [10].

If, in setting up an actual interferometer, satellites appear on moving the reflector, those which may be due to the reflector disclose themselves as companions lying in a set disposition relative to the main peaks. These satellites in fact are set up by waves reflected from some point of the reflector for which the angle of incidence is equal to the angle of reflection. They therefore result from alternative paths whose "apparent wave-length" bears a fixed relation to the "true wave-length" (for normal reflection) at each peak.

After aligning the reflector and source along the axis any satellites which remain have a fixed "radial wave-length" unrelated to the true one, except fortuitously through the choice of tube width.

Such waves were first discussed theoretically by RAY-

LEIGH[11] and experimented upon — in the audible gamut — by HARTIG and SWANSON[12]. They became apparent in the experiments on sound waves progressing along tubes by introducing a difficulty in getting uniformly spaced nodes and antinodes after a certain threshold of frequency, dependent on the radius of the tube, had been exceeded in the source — usually a loud-speaker at one end — employed to excite it. To deal with these we must write the equation for transverse waves in cylindrical coordinates:

$$\frac{1}{r}\cdot\frac{\partial}{\partial r}\left(r\,\frac{\partial p}{\partial r}\right)+\frac{1}{r^2}\,\frac{\partial^2 p}{\partial\theta^2}+\frac{\partial^2 p}{\partial x^2}=\frac{\ddot{p}}{c^2} \qquad (19)$$

of which the solution is:

$$p = J_m(\beta r)\left[A\cos n\theta + B\sin n\theta\right] e^{\iota(\omega t \pm gx)}\,. \qquad (20)$$

J_m is a Bessel function and the coefficients

$$g^2_{m,n} = 1 - f^2_{m,n}/f^2\,.$$

Here g is a constant for the mode and m and n represent the order of overtones for modes having radial nodes and circular nodes and anti-nodes respectively. (The nodal patterns are in fact the same as those for a membrane fixed at its circumference, but the vibrations of the particles are in line of the direction of propagation instead of perpendicular to it). $f_{m,n}$ is the frequency corresponding to any node, f that of the wave propagated axially.

On Fig. 31 are shown: to the left the instantaneous deflections of a plane — or imaginary membrane — perpendicular to the axis, as seen from the side: in the centre, the corresponding isobars on this plane, viewed from one end:

to the right, the isobars as seen in a section of the tube parallel to the axis. The modes *m*, *n* are indicated by the suffixes of *P* on the figure.

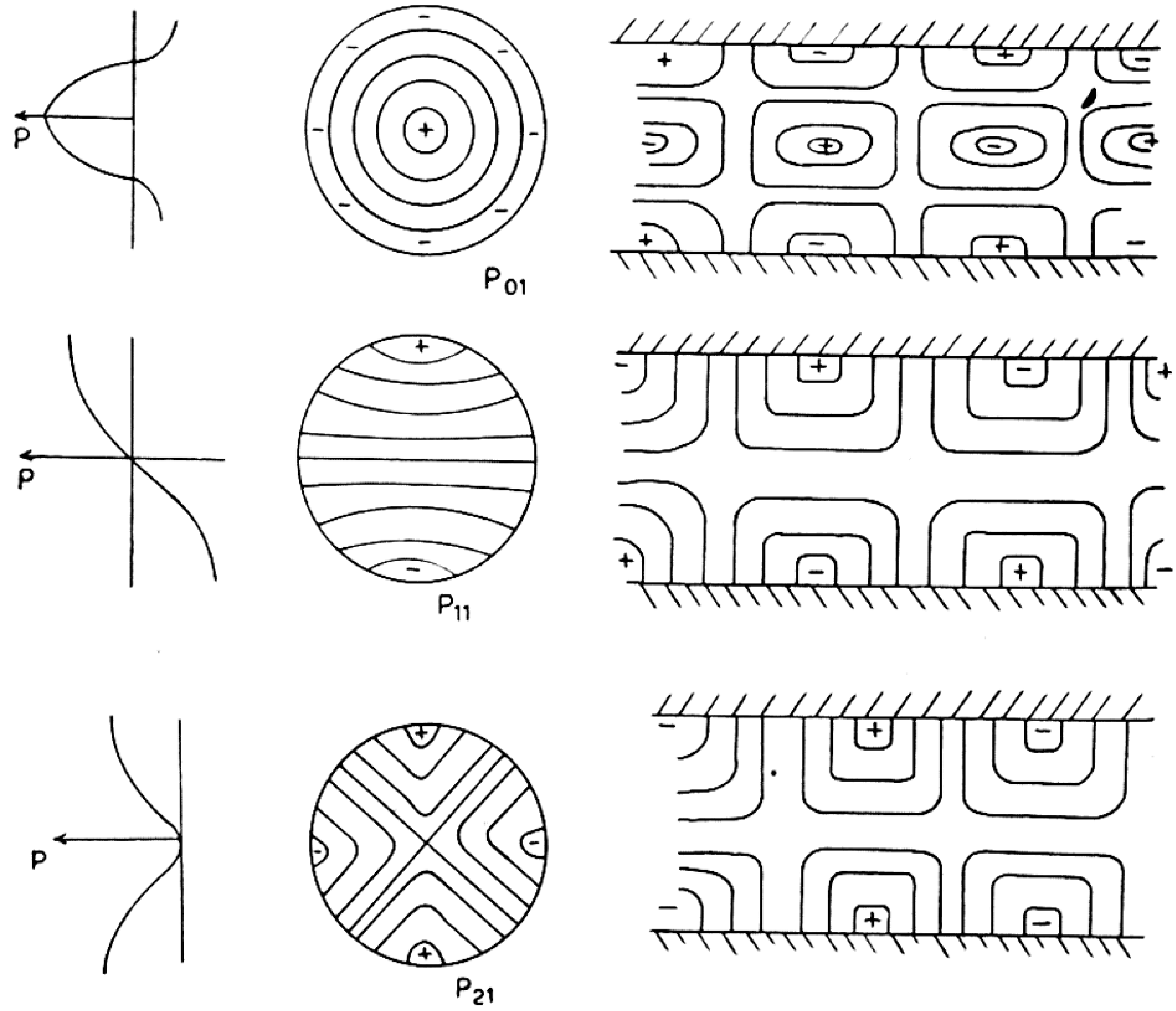

Fig. 31. Isobars of Modes of Circular Column

The resulting wave system in the pipe is then actually a three-dimensional one, for the radial and axial systems will interact, giving — for a given diameter and length of pipe — a pattern having nodal lines across the tube as well as down the tube.

It follows from equation (18b), and the appropriate solutions for the condition that the particle velocity at the boundary must be zero, that the velocities of the various radial partial tones depend on the frequency. The constant *g* really embraces this fact relating as it does the wave-length of the radial mode to that of the axial (plane) wave.

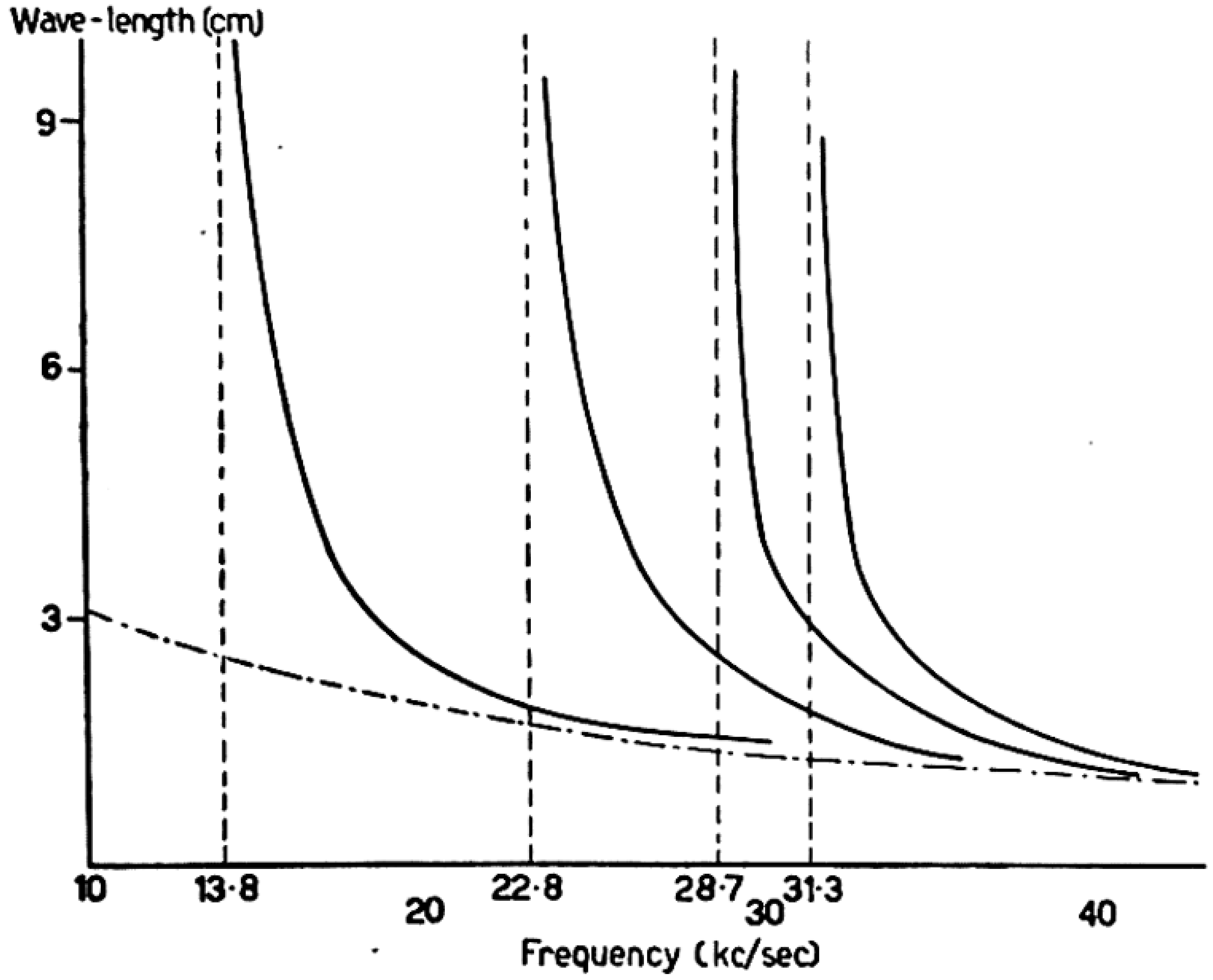

Fig. 32. Relation between Wave-length and Frequency in Tube

This is shown in Fig. 32 where the trend of this factor from its value at the threshold frequency (dotted line) to that of the axial modes is shown by the continuous lines. For comparison, the corresponding curve — part of a rectangular hyperbola — for the plane wave in an unconfined medium is shown as a chain line. Hartig and Swanson checked these effects by setting up several loud-speakers at one end of a tube (15 cm diam.) on the pattern shown in Fig. 33a and exploring the pressure amplitude not merely along the axis but also at points off it. Their apparatus is shown in Fig. 33b.

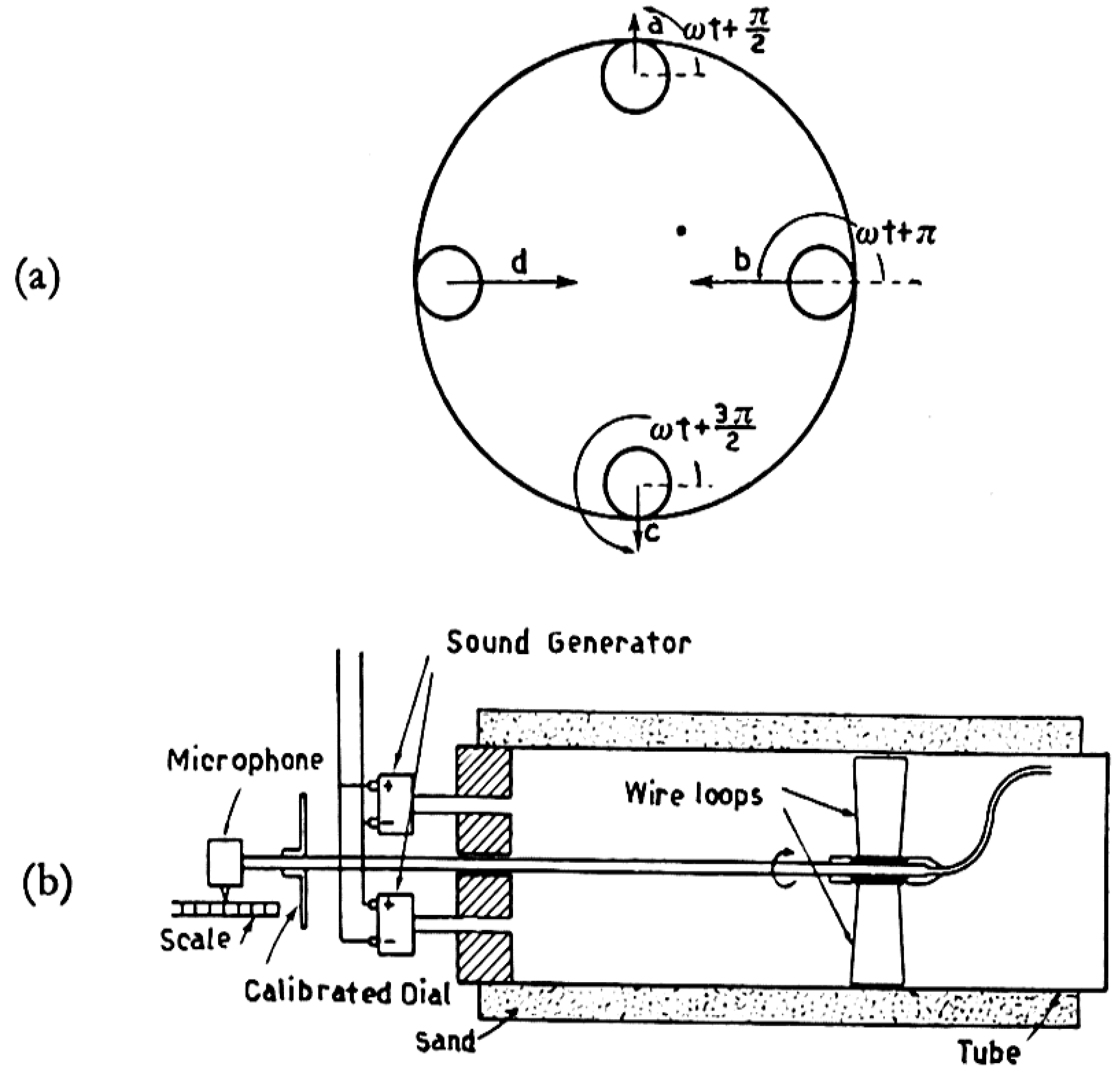

Fig. 33. Generation and Detection of Radial Modes of Sound Waves in Tube (Hartig and Swanson)

The four loud-speakers were set to produce the same frequency, but with different interphasal relationships, so to favour one or other of the radial modes of vibration illustrated in Fig. 31. A pitot tube can be moved along the tube at any set radial distance from the axis. From such results, isobars like those of Fig. 31 can be constructed.

In an ultrasonic interferometer then, we may expect to strike resonances as we move the reflector in this complex system, some due to the axial waves and some due to the cross components. In some instances these will constitute peaks clear of each other; in others they will intermodulate;

while below the threshold frequency at which the gravest cross-mode can be excited, the waves will pass down the tube as plane and no wall-effect or satellites will be observed.

In most modern interferometers, the satellites are reduced either by having a wide tube and packing the walls with absorbent material, so spoiling the terminal conditions of the radial modes and smudging them, or working with a narrow tube and frequencies below the threshold. The latter expedient may, however, produce complications by modifying the propagation constants of the waves by introducing viscous damping (*cf.* Chapter IV).

A method of sorting out the absorption α' due to these radial resonances from α, the true absorption in the gas has been suggested by KRASNOOSHKIN[13] who points out that in theory α is proportional to the kinematic viscosity and so inversely to the pressure on the gas. If results in an interferometer while the pressure on the gas is varied be plotted in the form: absorption against reciprocal of pressure, the slope of the straight line which should so be obtained has an intercept on the ordinate axis equal to α' for that particular wave-length. An example of such analysis will be made in the next chapter.

6. Viscous Damping in Narrow Tubes

If P is the pressure amplitude of a simple harmonic force acting along a tube of radius r_0, the equation of motion of an annular ring at radius r:

$$P = \left[\iota\omega\varrho - \frac{\eta}{r} \cdot \frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right)\right]\dot{\xi}$$

of which the solution is

$$\dot{\xi} = -\frac{P}{\eta\psi^2} + AJ_0(\psi r),$$

where $\psi^2 = -i\omega/\nu$ and J_0 is the Bessel function of zero order, ν standing for the kinematic viscosity coefficient, η/ϱ.

Integrating for the mean velocity over the tube and making $\dot{\xi} = 0$ at $r = a$

$$\bar{\dot{\xi}} = -\frac{P}{\eta\psi^2}\left[1 - \frac{2}{\psi a} \cdot \frac{J_1(\psi a)}{J_0(\psi a)}\right]. \tag{21}$$

When $\sqrt{\left(\frac{\iota\omega}{\nu}\right)} \cdot a > 1$ the whole tube is a "laminar boundary layer" in the sense of Poiseuille's law and the resistance $(P/\bar{\dot{\xi}})$ is $8\eta/a$. When $1 < \sqrt{\left(\frac{\iota\omega}{\nu}\right)} \cdot a < 10$, the commoner case in ultrasonics, the resistance becomes

$$\frac{P}{\dot{\xi}} = \iota\omega\varrho + (1 + \iota)\frac{2\sqrt{\eta\varrho}}{r}. \tag{22}$$

Taking this with (19) and the sound equation

$$P = \varrho c^2 \frac{\partial^2\xi}{\partial x^2}$$

we get

$$\left(\varrho + \frac{1}{r}\frac{\sqrt{2\eta\varrho}}{\omega}\right)\ddot{\xi} + \frac{1}{r}\sqrt{2\eta\varrho\omega} \cdot \dot{\xi} = \varrho c^2 \frac{\partial^2\xi}{\partial x^2}. \tag{23}$$

Assuming a S.H.M. solution, corresponding to a damped wave along the axis of x we obtain:

$$a = \frac{1}{rc}\sqrt{\frac{\omega\nu}{2}}; \qquad c' = c\left(1 - \frac{1}{r}\sqrt{\frac{\nu}{2\omega}}\right)$$

for the absorption and velocity in the tube, c being the free-space velocity.

7. Pulse Methods for Propagation Constants

We have already referred (p. 18) to the possibility of exciting a piezo-electric or magneto-striction oscillator into the emission of a short train of waves — at its natural frequency — by means of a "square-wave generator". This makes it possible to send a train of waves through the medium and catch it on an exactly similar crystal or — since to fashion such a pair is difficult — to let it be reflected and returned to the source which has meantime ceased to emit and been so connected as to form a detector of the retrogressive wave train. This was, in fact, the basis of the first ultrasonic application in which LANGEVIN and FLORISSON used the piezo-electric quartz oscillator to detect solid reflectors in the sea, and to measure their distance from the source by the time which elapsed between the commencement of emission and the reception of the echo.

The pulse and echo device was first used by BIQUARD and AHIER [14] as a means to study the properties of the fluid rather than of the reflector. In the laboratory, the distance of the reflector from the source is naturally small; so therefore is the time to be measured. It is usual to exhibit on a double-beam cathode ray oscillograph a proportion of the potential from the square wave generator as applied to the quartz, and from the quartz again as it receives the returning pulse. If the electron beam is being swept across the screen in the usual fashion while the experiment proceeds and is compared with (on the second beam) the ticks of a standard signal generator, the required time of passage of the pulse may be derived (see Fig. 34).

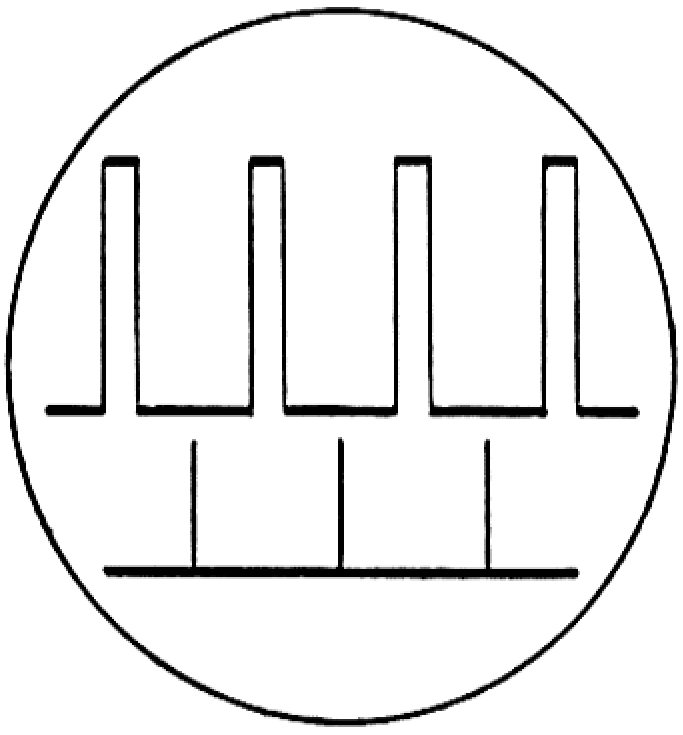

Fig. 34. Pulse Emission (Above) and Echo Detection (Below) (LENIHAN)

It is somewhat more difficult to derive the absorption coefficient for the medium since one must then have a signal on the oscillograph which is exactly proportioned to the pressure amplitude in the train of waves arriving back at the emitter. This can be done by suitable circuits and it is possible to calibrate the system by exposing the quartz to continuous ultrasonic radiation in which the pressure amplitude has been independently derived by the use of one or other of the detectors described in the preceding chapter.

Pinkerton[15] has successfully used the pulse method for absorption coefficients in liquids (p. 168). Of course, one does not avoid any of the corrections we have discussed in this and the preceding chapter by using short trains of waves instead of continuous radiation[16].

Actually, a series of pulses arrives at the source by ricochet between it and the reflector. These have amplitudes which diminish in geometrical progression. Satellite reflections may also arrive from the container walls unless these are lagged.

There is another distinction between pulse and continuous wave types of excitation. A pulse resolves by Fourier analysis into a group of waves embracing a small range of frequency Δf and the recorded time of return of the wave train will be appropriate to the velocity U of a group, rather than that c of simple harmonic motion. As long as the phase velocity c is independent of frequency the distinction is irrelevant but if — as occurs in some media — f/c is not constant, we shall have

$$\frac{1}{U} = \frac{\partial}{\partial f}\left(\frac{f}{c}\right)$$

representing the velocity of propagation in a "dispersive" medium of a group of waves of nearby frequency. The signal is reproduced then as the resultant of interference in the interval of time τ, the waves occupying a length L, related to the spread of wave-length by

$$\Delta f = \frac{1}{\tau}; \qquad \frac{1}{L} = \delta\left(\frac{1}{\lambda}\right).$$

The difference between the velocity of the group and that of "monochromatic" waves is then given by

$$\frac{1}{U} - \frac{1}{c} = \frac{f}{c^2} \cdot \frac{\partial c}{\partial f}. \tag{24}$$

In order to show dispersion the pulse must be so long that it covers a range of frequencies in this way, but not so long that it is, in effect, monochromatic. For a train of 2 megacycles/sec lasting 5 microseconds, $\Delta f/f$ amounts to 10 per cent. and would suffice to detect a dispersion of velocity, if such existed, of about 2 m/sec at that frequency.

8. Velocity in Liquids by Optical Methods

In the preceding chapter we have remarked on a faculty of ultrasonic waves, if the compressions along their fronts are sufficiently intense, to diffract light or cast shadows (p. 43). In progressive or stationary plane waves, this property may be made of use to measure the ultrasonic wave-length.

We shall consider first the application to this purpose of the shadow or schlieren methods, as their technique is simple, especially if stationary waves are set up. This was much developed in the period 1931 - 39 by HIEDEMANN [16] and his collaborators in Cologne. A considerable portion of the ultrasonic field in a liquid is illuminated by a beam of monochromatic light which cuts across it perpendicularly. The nodal planes then appear as dark shadows when viewed from the other side of the trough containing the liquid, in spite of the fact that they are seats of rapidly varying (optical) density, whereas the density remains normal in the antinodes. The reason for the visibility of the nodes is to be sought in the fatigue of the eye, and the fact that the fluctuations remain localised, do not move about in the liquid.

To adapt the same technique to progressive waves requires that one should interrupt the light at the same (ultrasonic) frequency as the source in order that the places of excess density may *appear* to be stationary. This is easy if one employs a Kerr cell, *i.e.*, a glass cell containing a liquid such as nitrobenzene which becomes doubly-refracting when a potential is applied to it and so can be used as a shutter for polarised light. The monochromatic light is first plane-polarised by being passed through a Nicol prism, passes then through the Kerr cell and the ultrasonic trough to fall on a second Nicol prism which can be turned — the electric circuit being inoperative, meanwhile — so that the light is completely cut off. If now the quartz is excited and some of the potential from its driving circuit applied to the electrodes of the Kerr cell, the nitrobenzene will let through some light once in each oscillation of the quartz, since its exciting potential is tapped off the latter, and so give stroboscopic glimpses of the ultrasonic wave-fronts which then appear visible, (*cf.* Fig. 35).

It is to be noted that in both applications, the variation in density from place to place along the beam is sinusoidal and not step-wise or castellated. However, the light is moving athwart a stratified medium — in the optical sense — and so tends to be refracted away from the denser layers, leaving a region in shadow behind the most dense part of the wave-front. We therefore get much sharper shadows of the nodal planes, or fronts of compression, as the case may be, than we should deserve to get, if the nodal planes were merely nodal lines, without depth and the consequent possibility of refraction.

An even simpler apparatus, suitable for a lecture demonstration, has been set up by Fox and Rock[18]. No lenses or slits are used, but the light source is a straight discharge tube containing mercury vapour from which the light passes athwart an ultrasonic oscillator which modulates the source with its own frequency, then through the liquid in a trough which is irradiated at the same ultrasonic frequency. A screen placed on the other side then receives shadows of the compressions in the progressive waves which are "held" in position by the interrupted light of the same frequency. Thus the optical system is just like that which is used to measure the wave-length of low frequency ripples on a liquid, in which experiment the tuning fork which originates the ripples by dipping into the surface also interrupts synchronously the light by which they are viewed, giving the ripples a stationary appearance. A feature of this optical system is its simplicity which makes adjustment for plane-parallel light unnecessary and allows of the calculation of the wave-length in terms of geometrical constants which can be measured accurately. It is necessary to eliminate standing waves in the trough. This is done by making the radiation pass into a chamber at the end of the trough in which the energy is frittered away by repeated reflection between walls covered by gravel.

Though it is more difficult to measure wave-lengths in gases than in liquids by these methods, owing to the difficulty of getting sufficient ultrasonic amplitude to change the density effectively, this has recently been done by PETERSON [16] and BÖMMEL [17] (p. 114). In all cases, the region immediately in front of the source is avoided as the temperatures or gradients of temperature there set up vitiate the readings.

9. Ultrasonic Wave-Train as Optical Grating

About thirty years ago, BRILLOUIN [19] predicted that, if a liquid were penetrated by progressive waves of compression of short wave-length and at the same time were irradiated by light, the regular pattern of density variations in the liquid could act towards the light in the same way as a diffraction grating or as a crystal acts towards X-rays. Thus in Fig. 35 suppose that a sinusoidal procession of compressions and rarefactions is moving in the direction XX' giving at the instant pictured maxima of compression distant d apart at A,A' and interspaced rarefactions, B,B' and let light of wave-length l be incident at an angle i

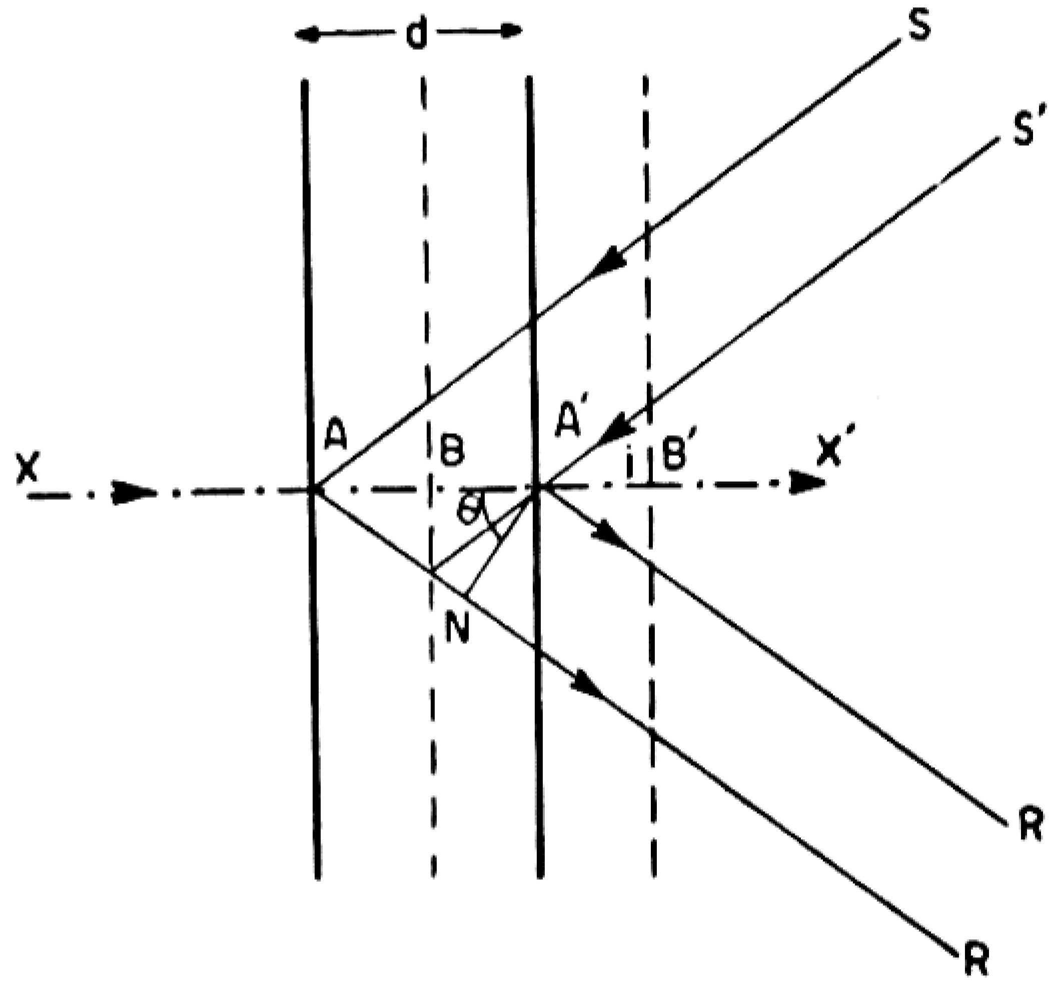

Fig. 35. Diffraction of Light by Plane Sound Waves

to the direction of propagation and be diffracted along paths such as SAR, making an angle θ to XX'; then the optical path difference is $d(\sin i + \sin \theta)$. Whenever

$$\pm l = d(\sin i + \sin \theta) \tag{25}$$

there will be consonance in the two paths of light reaching a lens and screen collecting the light at points R, R' on a perpendicular to the rays after diffraction in the direction θ. The student of optics will note that we have introduced a simplification into the diffraction formula, comparing it with that of the line or crystal grating, in that we have allowed only of two diffraction maxima in place of the multiple "orders" permitted by the general grating theory. This has been done of set purpose for it is a consequence of the sinusoidal nature of the "rulings" of the grating and compares with the same modification we had to make in the last section when exploring the shadow or schlieren field of an ultrasonic beam. He will also note that the "grating" is virtually being shot at the speed of sound through the "spectrometer" while the diffraction pattern is being studied, but should be able to appreciate that this does not invalidate our assumption that the diffraction spectrum will be stationary, the speed of light being, by comparison, so high. We may also note, that, in practice, the light beam will be incident parallel to the ultrasonic wave-front, *i.e.*, $i = 90°$.

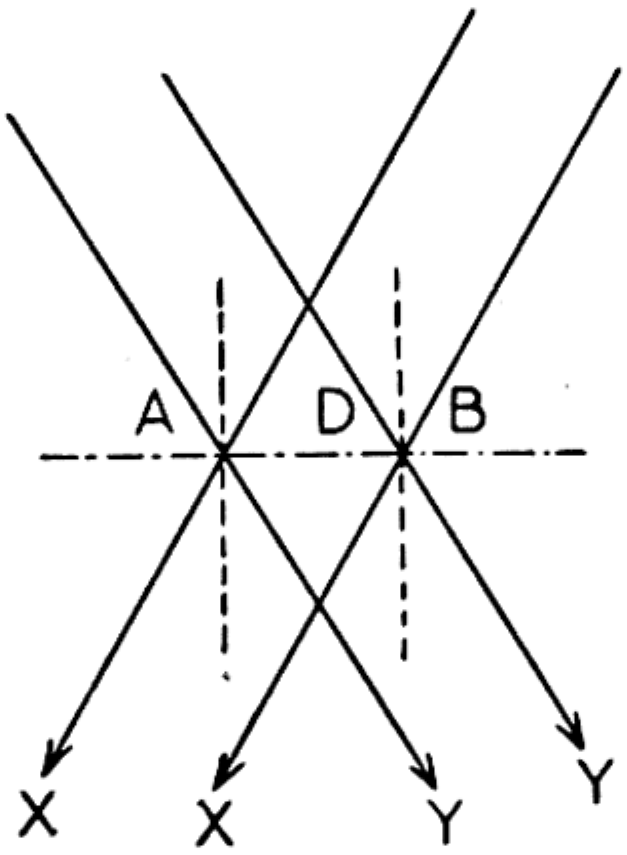

Fig. 36. Explanation of Optical Diffraction by Sound Wave

The theory of an optical grating in which the lines have a blackness varying sinusoidally or in which the glass varies in thickness sinusoidally was also discussed as an academic exercise in some of the nineteenth century text-books on optics from which one can derive a formula, in this fashion: The effect of two maxima of diffraction one on either side of the central beam can be achieved by letting two beams cross, as in Fig. 36, and calculating the resulting distribution of amplitude across AB. Since the phase across AB is everywhere the same, that at any point D is as much in advance of one wave-front as it is behind the other, and the amplitude of each wave being the same:

$$\xi = a \sin(\omega t + \delta) + a \sin(\omega t - \delta) = (2a \cos \delta) \sin \omega t\,.$$

The resultant amplitude across AB is then given by the term in brackets wherein $\delta = 2\pi\, x/l \cdot \sin\theta$, x being distance along AB. Thus AB represents a resultant wave-front of uniform phase but over which the amplitude shows a sinusoidal variation such that where $x = l \operatorname{cosec}\theta$ the configuration repeats: this quality is in fact the spacing of a grating which will give the distribution of light (beyond the grating) of Fig. 36.

If the grating has "thickness" in the direction of the light beam, the amplitude is as follows, corresponding to the central maximum and two orders of diffraction:

$$\xi = a_0 + a_1 \cos 2\pi\, x/l \cdot \sin\theta + a_2 \cos 4\pi\, x/l \cdot \sin\theta\,. \quad (26)$$

It was not until the advent of ultrasonics that it became possible to put this formula under test and to use it to measure the ultrasonic wave-length in liquids in terms of the light wave-length. The experiment was done independently by LUCAS and BIQUARD [20] on the one hand and DEBYE and SEARS [21] on the other in 1932. A simple set-up for such an experiment has a quartz of about 300 kc/sec driven by a Hartley circuit and radiating into a liquid contained in a glass-sided trough through the side of which the light from a sodium lamp, after having been rendered parallel and directed through a slit. traverses the ultrasonic beam at right angles. On looking through a telescope of short focus on the far side, the light will be seen separated into the direct ray, bordered by diffraction maxima and minima.

Sometimes only the two maxima of the theory are observed according to (25) but more often unexpected clusters of lines appear even with monochromatic light and monotonous ultrasonics.

The origin of these "spurious lines" has been much debated, particularly by RAMAN and NATH [22] and by PARTHASARATHY [23] in a series of papers. Their interest is rather from the optical than the ultrasonic aspect, so we shall content ourselves with a brief summary of their ideas on this subject. In an experiment BÄR [24] showed, by obtaining mutual interference when the spectra of higher order were brought into confluence, that they are due to multiple passages of the light from side to side of the trough threading through the "grating" and so suffering multiple diffraction. RAMAN and NATH seized on this idea, gave it mathematical formulation and were able not only to calculate the positions but the relative intensities of the extra orders. They were also able to explain an observation of DEBYE and SEARS, *i.e.*, that when the angle between the incident light and ultrasonic beams is gradually inclined from the normal 90° the intensity of the diffracted light passes through a waxing and waning of intensity. Thus, considering (Fig. 37a), a plane wave-front XY of uniformly illuminated light passing through the trough, in which at the instant figured the parallel lines represent the maxima of compression, we should expect that on emergence the optical wave-front X′Y′ would show variations as indicated. At (b) where the light is more inclined, the light waves cut partly athwart rarefactions, while at (c) there will be no path difference in the two light rays indicated by chain lines, and so the phase difference vanishes. This will, in fact, occur whenever $\tan\theta$ is l/L, L being the width of the trough.

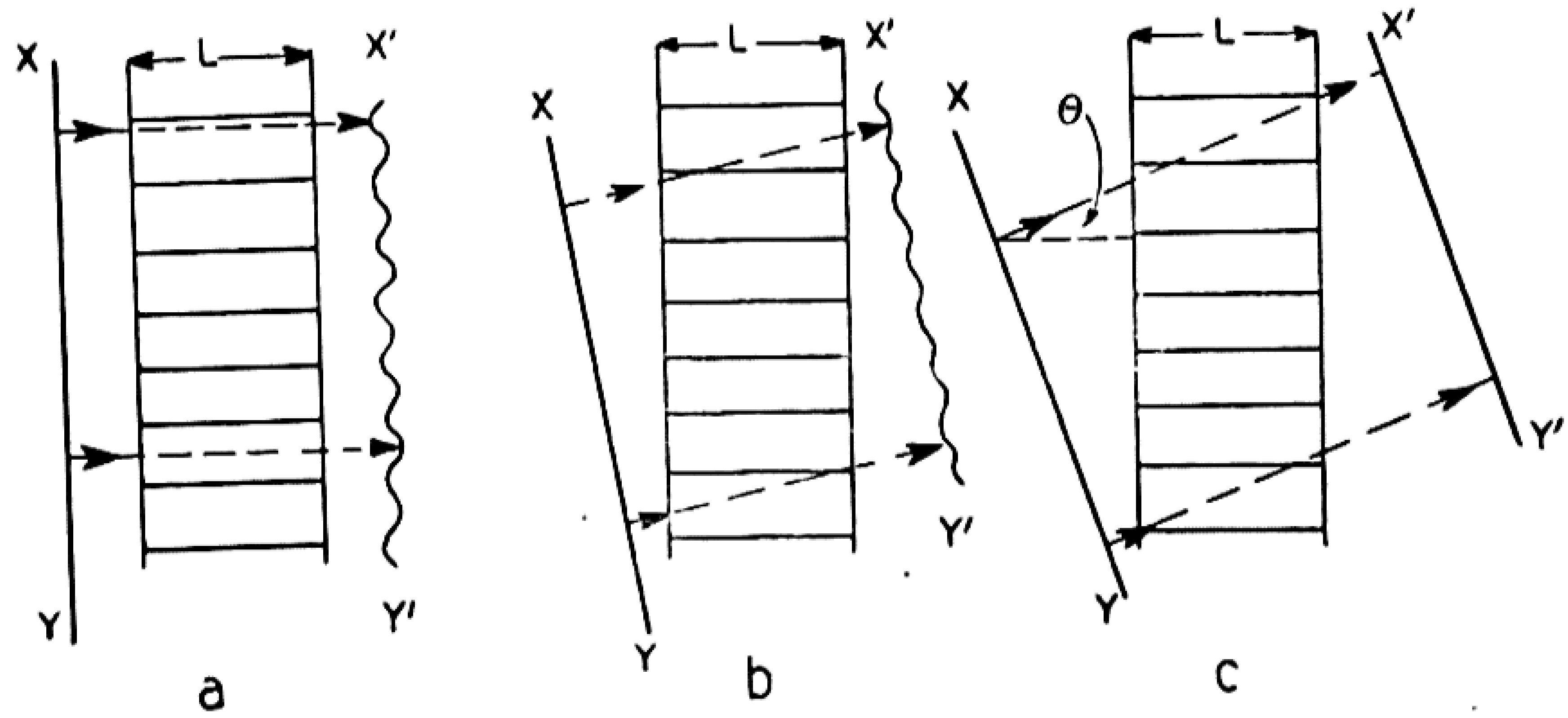

Fig. 37. Optical Diffraction by Extended Wave-Front

The deviations from the simple theory are mainly due to the finite "thickness" of the grating and its effect in refracting the waves within the grating and to a Doppler effect, noted by ALI [24], whereby the emergent light into an order m of diffracted maximum is modulated from its frequency by a term $\pm mf$, where f is the ultrasonic frequency.

The presence of these unwanted spectral lines complicates the application of the BRILLOUIN method, though, fortunately, they are of higher order and less luminous than the first order maxima. Provided one ensures parallel incident light and a strictly moderate ultrasonic intensity, it is a very convenient method for measuring ultrasonic wavelengths in liquids and most of the results of velocity to be reported in Chapter V have been obtained in this way. Little success has attended the attempts to operate the principle in gases for the reason with which the reader is now familiar.

Attempts, too, to use it for absorption have not been fruitful. These have resolved upon the possibility of measuring the relative luminosity of the diffracted light, blocking out the direct illumination, at different stations along the ultrasonic beam as it passes through a column of the liquid. BIQUARD [25], GROBE [26] and BAZULIN [27] have each tried to do this using photo-electric cells to measure the light intensity, and making the assumption that the intensity of the first diffraction maxima is proportional to the *ultrasonic* intensity at the plane of intersection of light and sound beams. In view of the difficulties in measuring luminosity in a narrow line and the complexities of the theory of the whole phenomenon (*vide* RAMAN-NATH) it is scarcely surprising that their results for absorption coefficients are inconsistent with those obtained in other methods as well as among themselves.

Owing to the obliquity effect, the desired first order maxima become weak at very high frequencies. Thus, as BHAGAVANTAM and RAO [28] point out, if λ has become so small that, at minimum deviation light incidence,

$$\frac{\lambda}{L} \simeq \tan\frac{\lambda}{L} = \sin\frac{\lambda}{2\mu l} \simeq \frac{\lambda}{2\mu l},$$

μ being the optical refractive index, there will be no light in the first order diffraction; even less at normal light incidence. A feeble revival of intensity may occur at still smaller ultrasonic wave-lengths but there will again be cancellation when $2\mu l = \frac{1}{2}L$, but the conditions will scarcely repeat themselves at higher frequencies. BHAGAVANTAM and RAO were able to get feeble spectra at 50 Mc/sec. For the lower limit of applicability of this technique, one could take 6 Mc/sec, at which frequency in water using sodium light, the first order occurs at about 2°.

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CHAPTER IV

PROPAGATION IN GASES

1. Low Frequency Measurements

It is desirable before describing the high frequency work to pass in review the earlier measurements at audio frequencies since these give, especially as regards velocity, data with which to compare the newer data and the opportunity to look for dispersion — variation of velocity with frequency — or any abnormally large attenuation at high frequencies.

The basic method at low frequencies, from which indeed the ultrasonic interferometer stems, is that of Kundt's tube. The source of sound used by KUNDT [1] and most of his followers was a wooden or glass rod excited by friction into longitudinal vibration. Owing to the high speed of longitudinal waves in such solids, the note is already fairly high in the audible range when a rod several feet long is used. If quite short rods are used, it is even possible to push the frequency into the ultrasonic region. Nowadays, however, the rod is often replaced by a loudspeaker diaphragm. KUNDT then tuned the air in the tube to the rod, by adjusting the position of a reflecting stopper in the tube, and observed when resonance was attained by strewing dust or a light powder along the floor of the tube laid horizontally. He thus compared the wave-lengths in air and the solid for the same frequency.

By introducing other gases into the tube it is possible to obtain values of the velocity in these gases. An objection to doing this is that the free passage which must be left for the rod to vibrate in will permit the outside air to diffuse into the tube. Another arrangement due to KUNDT is to place a second tube at the other end of the rod containing the gas and some dust. When the note in the rod is excited, both tubes are adjusted to resonance and the ratio of the wave-lengths in the air and in the gas, measured from the dust figures, gives the ratio of the speeds of sound. The latter ratio gives important information on the molecular structure in the gas, as the ratio of the specific heat of the gas at constant pressure to that at constant volume is a definite function of the number of atoms which go to make up the molecule.

In order to enable a chemically purified gas to be kept from contamination by the outer air, BEHN and GEIGER [2] introduced the ingenious improvement of enclosing the gas itself in the rod which is rubbed to produce the note. To this end the rod is made hollow and of glass, and contains dust. The gas is introduced at the mid-point which is clamped. The column of gas in the rod is of invariable length and may therefore not resound to the note in its glass container, but the effective length of the rod is increased by screwing on metal washers to a threaded metal extension-piece at each end of the rod, until the dust inside shows that resonance has been reached. The adjustment is thus the reverse of what it was in the original apparatus, since here the rod is adjusted to resonance with the gas. It is usual to retain the air-tube, and, after the first adjustment, to adjust this for resonance. Wave-lengths and velocities in the two gases can then be compared. The BEHN and GEIGER apparatus has been much used by other chemists and physicists, notably by PARTINGTON.

KUNDT's method provides the possibility of measuring the velocity of sound in gases at different temperatures, if the tube be surrounded by a thermostat. At low temperatures it would be inconvenient to surround a long tube by liquid air, but HIMSTEDT and WEDDER [8] have been able to measure velocities at low temperatures, by using a very high-pitched source of sound in place of the glass rod, requiring only a short length of the gas-tube accommodated in a Dewar vacuum vessel. In this case resonance in the column of gas was detected by a microphone at the bottom of the gas-tube, which was of invariable length. The frequency of the note given by the whistle, when the gas was thrown into maximum vibration, was determined by a subsidiary Kundt's tube containing air.

In all these "tube-methods" a correction to the velocity of sound as observed is necessary for the frictional effect of the gas on the tube walls, to derive therefrom the velocity in unconfined gas.

When absorption by a gas is in question, the use of a tube of reasonable length *at low frequencies* is not feasible, as the absorption of sound in every known gas falls beyond the limit of detection by Kundt's method. Instead the resonance curve of a cavity containing the gas is measured by subjecting it to various frequencies, and recording the response of the gas, as OBERST [4] did at sonic frequencies in a tubular resonator. He placed a loud-speaker at one end and a carbon microphone at the other, and so obtained the resonance curve of the system in air. We shall notice an application of this to other gases later (p. 115).

The instrument known as the hot-wire microphone may be used for this purpose. TUCKER [5] has used this in a double form consisting of two reservoirs connected by a narrow neck in which is located the hot-wire grid whose change of resistance with tuning measures the response of the system. Measurements were made of the natural frequencies of the system, which were in the neighbourhood of 200 c/sec, when the resonator was filled successively with air — at various temperatures — carbon dioxide and hydrogen. From the Q of the resonators, comparative values of absorption in the gases could be calculated. Evenso, the resonance curve of such a resonator is very sharp, owing to the small damping, which may indeed be due rather to the materials of which the walls of the cavity are lined than to the gas.

2. Ultrasonic Propagation in Pure Gases

In an ordinary gas the velocity is independent of frequency but the absorption increases in proportion to the square of the latter[7]. We may, in fact, write — for plane waves —

$$\ddot{\xi} = c^2 \frac{\partial^2 \xi}{\partial x^2} + \frac{4}{3} \nu \frac{\partial \xi}{\partial x}$$

in which ν is the kinematic coefficient of viscosity[6], enhanced by a contribution, which has been shown to be the equivalent of a $\frac{1}{3}$ increase over the value appropriate to undirectional flow. Taking a simple harmonic solution,

$$\xi = a\, \mathrm{e}^{-\alpha x}\, \mathrm{e}^{\iota\omega(t - x/c)}$$

we find for the attenuation factor:

$$\alpha = \frac{2}{3} \frac{\nu\omega^2}{c^3} = \frac{2}{3} \frac{\nu K^2}{c} = \frac{8\pi^2}{3} \cdot \frac{\nu}{\lambda^2 c} \quad . \tag{27}$$

When heat conduction is considered we must enhance the term $\frac{4}{3}\nu$ in this equation by a factor $\left(\frac{C_p}{C_v} - 1\right) \frac{K}{\varrho C_p}$ where K is the thermal conductivity of the gas, and C_p and C_v are the specific heats at constant pressure and volume respectively.

For a non-dispersive gas, then, $\alpha\lambda^2$ should be constant. This is often called the Kirchhoff constant. As gases have kinematic viscosities of the order of 0.15 $\mathrm{cm^2 sec^{-1}}$ and velocities of order 300 m/sec, this constant wavers about $2 \cdot 10^{-4}$/cm.

NEKLEPAJEV[8] was the first to use frequencies high

References pp. 155–157

enough for the detection of α in free space as an excess over the usual decrease of intensity with the inverse square of the distance from the source. He used the sound from an electric spark as source, whereby he produced sounds of wave-lengths of about 1 cm in air. These were concentrated by means of a mirror onto a sound-grating and, after diffraction and re-focussing in another mirror, on to the radiometer which gave the intensity at this point. He found $7.3 \cdot 10^{-4}$ for α in place of the Kirchhoff $3.2 \cdot 10^{-4}$.

The first measurements with the PIERCE interferometer, continued by ABELLO [9], then by KNESER and by GROSSMAN, showed that while the velocities in diatomic and monatomic gases at N.T.P. were the same as at low frequencies, and the absorption, as represented by the Kirchhoff constant, only slightly greater than theory, yet a number of triatomic gases (notably carbon dioxide) exhibited a rising velocity within the ultrasonic gamut and an absorption many times the "classical" values.

The measurement of V by the Pierce interferometer is straightforward and all workers are in agreement. The velocity is usually reduced by a simple application of Charles' Law — *i.e.* $V/V_0 = \sqrt{T/T_0}$, where T represents the absolute temperature — to that corresponding to 0° C.

The case is rather different with absorption. GROSSMAN [10] used a "point-source" by letting the quartz radiate through a small hole into the gas and picked up the radiation at a distance r on another quartz, cut to the same frequency as the source. If I_1 and I_2 are the intensities at r_1 and r_2 respectively from the source: $I_1 r_1^2 = I_2 r_2^2$ in the absence of absorption. Otherwise

$$I_1 r_1\, e^{-ar_1} = I_2 r_2\, e^{-ar_2}$$

so that the Kirchhoff constant,

$$a\lambda^2 = \frac{\lambda^2}{r_2 - r_1} \cdot \log_e \frac{I_1 r_1^2}{I_2 r_2^2}\,. \tag{28}$$

We have already (Chap. III) outlined the conditions, laid down by HUBBARD and HARDY, for obtaining the absorption coefficient from the peak readings of anode current in the driving circuit of the quartz as the reflector is moved.

With the fixed-path interferometer using the hot-wire detector one may measure both V and a as indicated in the last chapter. This method used by the author[11] is as follows:

A nickel wire heated just below red heat, the resistance of which has been previously balanced in a simple Wheatstone bridge, experiences a small lowering of resistance, indicated by a change of the galvanometer deflection, when exposed to an oscillating quartz, piezo-electrically maintained, in a chamber sealed against draughts and lagged with asbestos felt to prevent reflection of the radiation.

The change of resistance which an electrically heated wire experiences when exposed to an alternating draught consists of two parts; (1) a steady drop of resistance; (2) a change alternating with the draught; there may also be variations harmonic to the fundamental frequency

(p. 40). The predominance of the second effect is favoured by low frequency and fineness of the wire. At these high frequencies, the effect is almost entirely of the first kind, the alternating effect being a very small ripple on the surface of a large steady fall of resistance. Moreover, it can be shown that when the temperature of the wire is sufficiently high, this drop is that which the same wire would experience if exposed to a steady wind of velocity $2\pi f\xi$ where f is the frequency and ξ the amplitude of the alternation. In the present research a nickel wire of diameter 0.001 inch was used, heated by a current of 0.1 amp.

The alternating current across the electrodes was measured by a thermo-galvanometer at the same time as the resistance of the wire, and it was assumed that in the dynamic piezo-electric effect as in the static effect, the longitudinal elongation of the crystal was proportional to the applied potential difference. A method to confirm the calibration curves was devised later.

In the application of the hot-wire to ultrasonic interferometry, either (a) the reflector may be held still, and the hot wire moved between it and the crystal (*cf.* theory on p. 12), or (b) the hot-wire can be stationary and the reflector moved. This affords a very sensitive indicator of wave-length; deflections of the galvanometer connected to the hot-wire could still be detected under circumstances in which no change in the current through the maintaining oscillator (Pierce method) could be detected. In gases like argon and oxygen (the latter under the proviso that the frequency is not too high in the ultrasonic gamut) the stationary waves are practically perfect sine waves, since the measured damping is quite small. Assuming this to be so, the measured resistance of the hot wire in such cases may be correlated with an assumed sine wave formation to act as a check on the calibration curves obtained by the earlier method. Results so obtained at 98 kc/sec are shown as crosses on the oxygen curve of Fig. 18 (p. 41). This method of calibration was suggested by some earlier work of PARIS in the audible gamut.

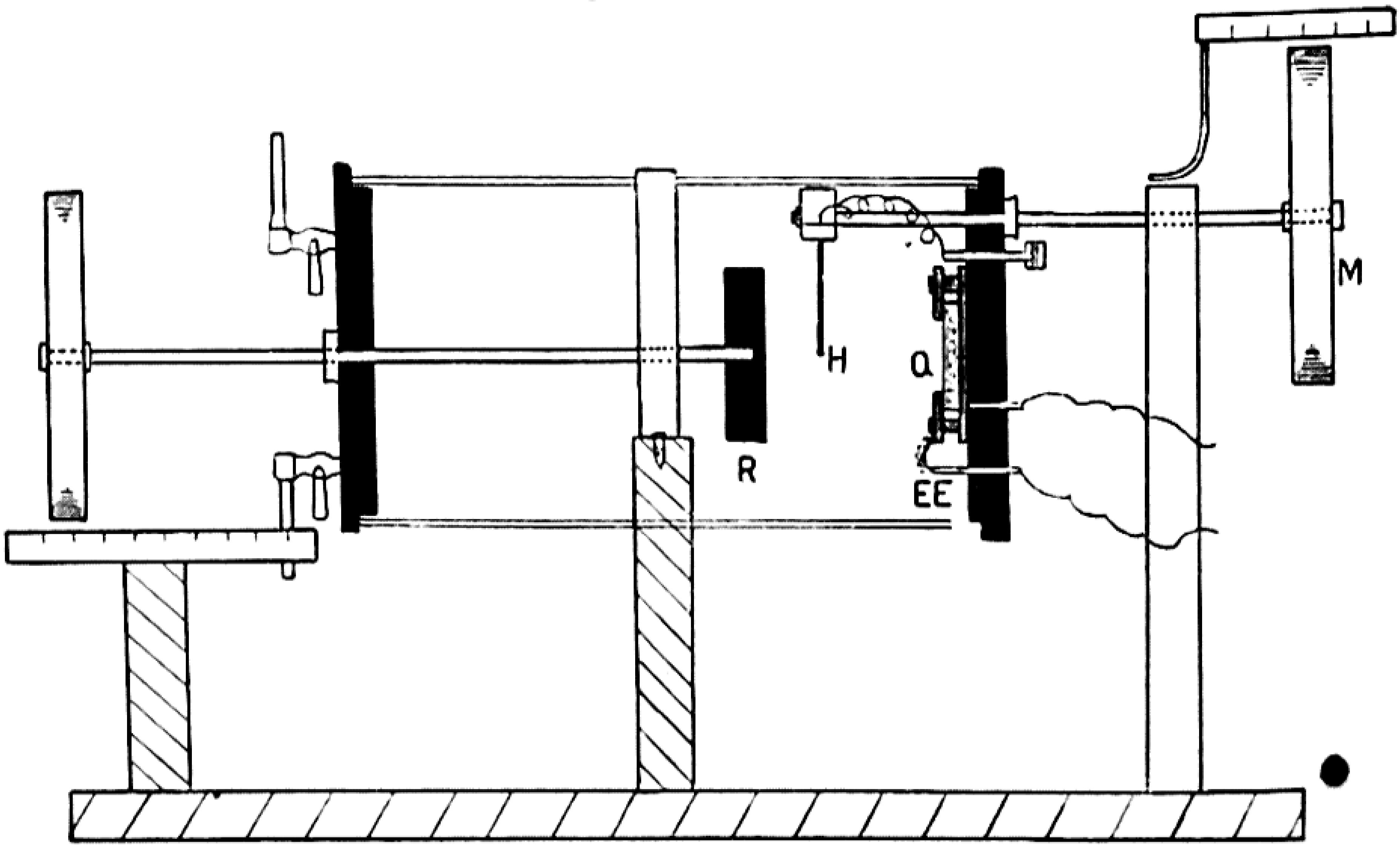

Fig. 38. Hot-Wire Interferometer for Gases (RICHARDSON)

The complete apparatus, as mounted for method (a) is shown in Fig. 38. The quartz *Q* is a disc vibrating in the direction of its thickness, held lightly between two polished brass electrodes *EE*, the outer of which has a hole 2 cm diameter cut in it to let out the radiation. (For frequencies below 500 kc/sec slabs oscillating along their length were used, the holder being modified so that the quartz lay between two horizontal electrodes.) This crystal holder was fixed to an ebonite disc which formed one cap of a glass tube 12 × 6 cm diameter. Through a gland in this cap passed the rod carrying the hot-wire H mounted on a fork of which the upper part is shaped to fit the tube in a way that it is merely carried forward or backward on turning the micrometer disc *M*, marked in degrees. The reflector R, also of ebonite, is carried on the end of a rod screwed through a gland in the cap fitted to the other end of the tube which also has three gas taps. Both rods, that carrying the reflector and that carrying the hot wire, are tapped with a fine thread and provided with large micro-

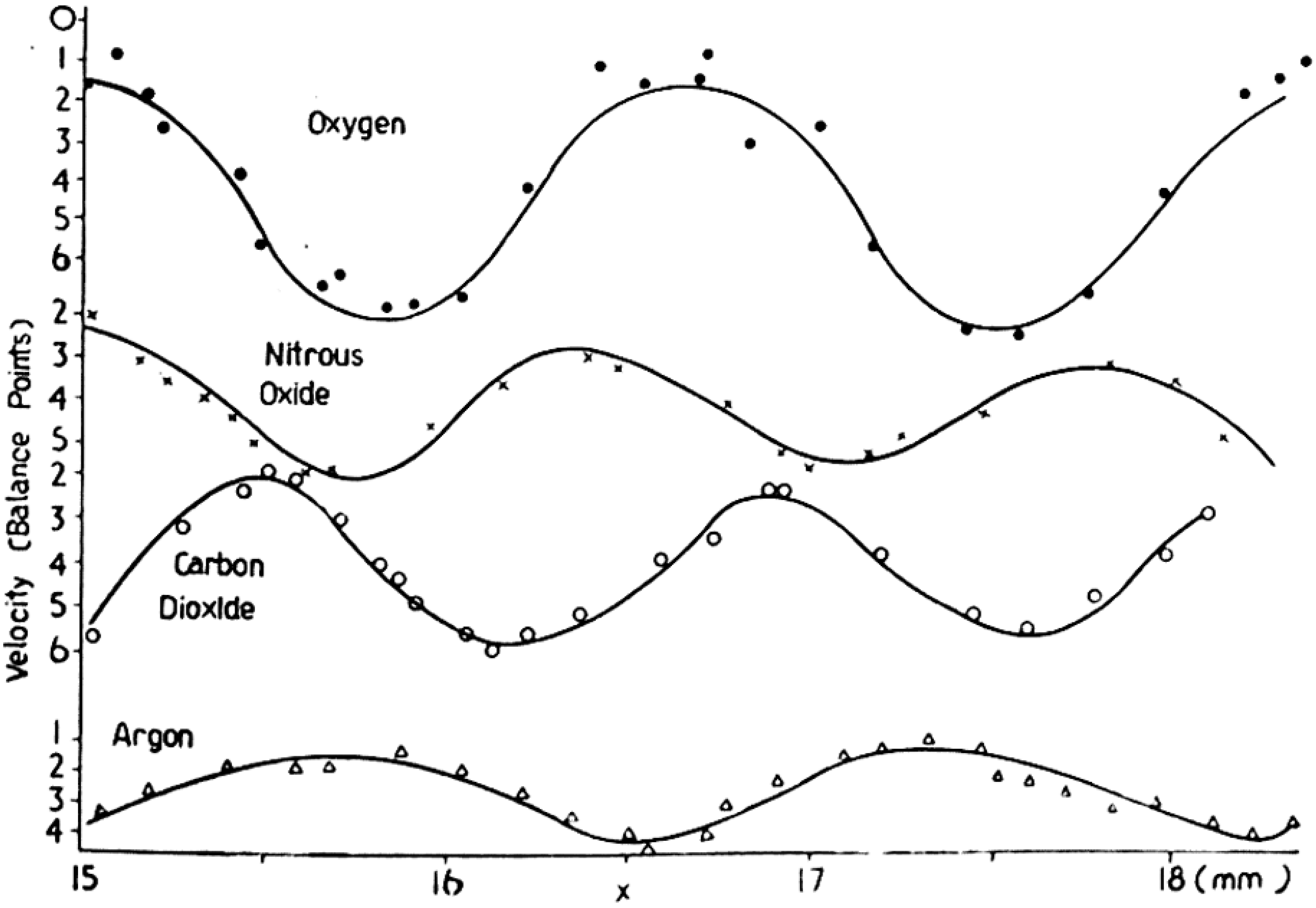

Fig. 39. Graphs of Particle-Velocity and Distance in Stationary Waves, for Four Gases

meter heads. The caps are sealed on with picein. In using the progressive wave method the reflector is removed and the far end of the tube is padded with a sound-absorbing composition of asbestos. With each quartz in position a test was made in argon to find whether any sound was radiated obliquely on to the sides of the tube. Such "spreading" was detected by an apparent decay of amplitude along the tube, such as one would not expect in this gas. As a matter of fact, with the fairly wide radiation orifices used,

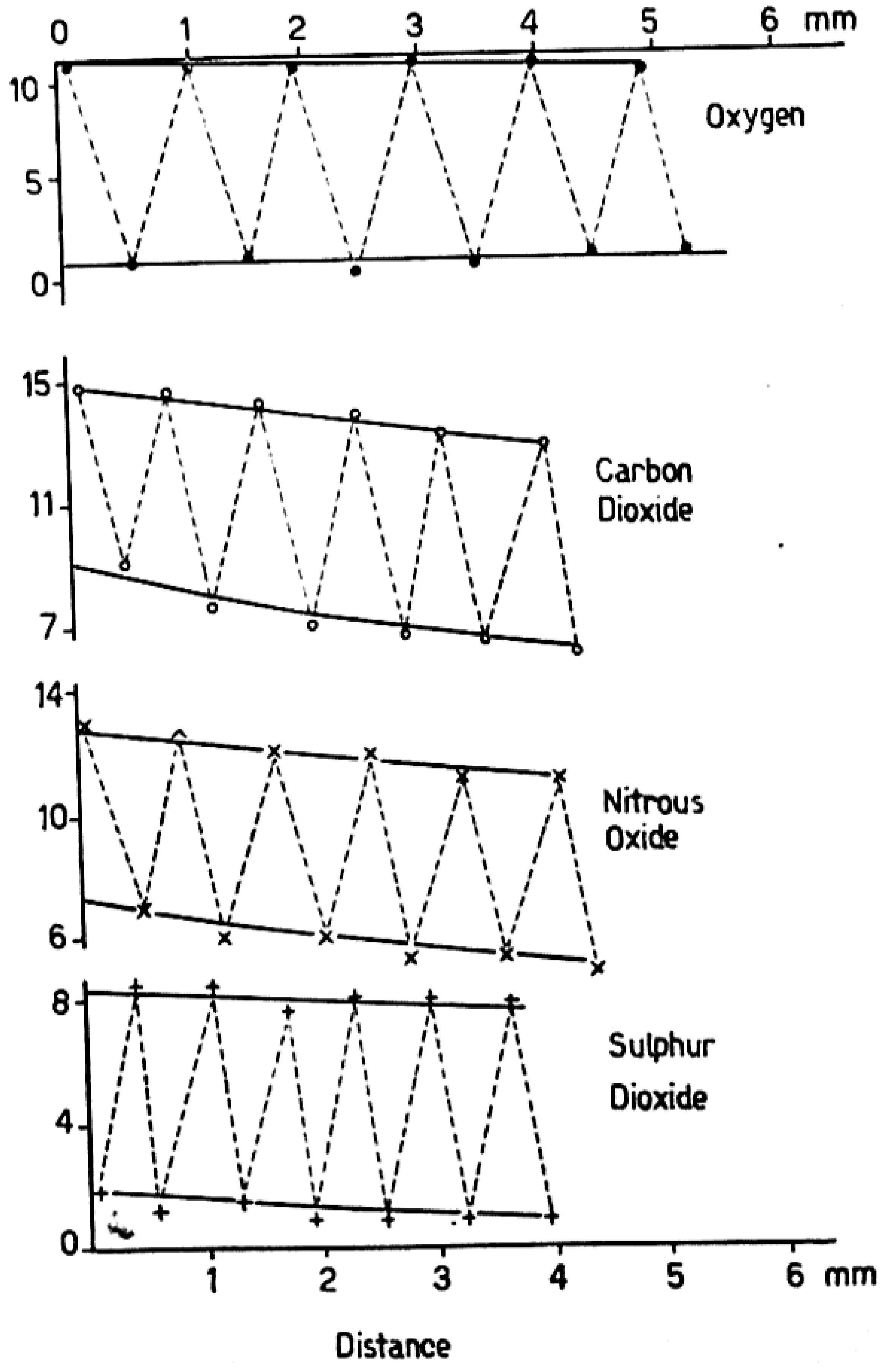

Fig. 40. Loci of Maxima and Minima in Pseudo-stationary Waves

spreading was appreciable only at the lowest (40 kc/sec) frequency in a normal gas.

The next two figures show results of the "stationary wave" measurements. Fig. 39 shows detailed results for a few peaks at 98 kc/sec, the recorded points being the actual hot-wire readings, while the lines drawn give the shape of the stationary waves after a small correction in the light of the calibration curves. On Fig. 40 (at 167 kc/sec) the maxima and minima only are shown, connected by dotted lines. The continuous lines give the general trend of these, from which the wave-length and absorption can be calculated. The change of amplitude with distance in carbon dioxide and nitrous oxide is well marked.

Fig. 41 shows the calculated results in the four gases.

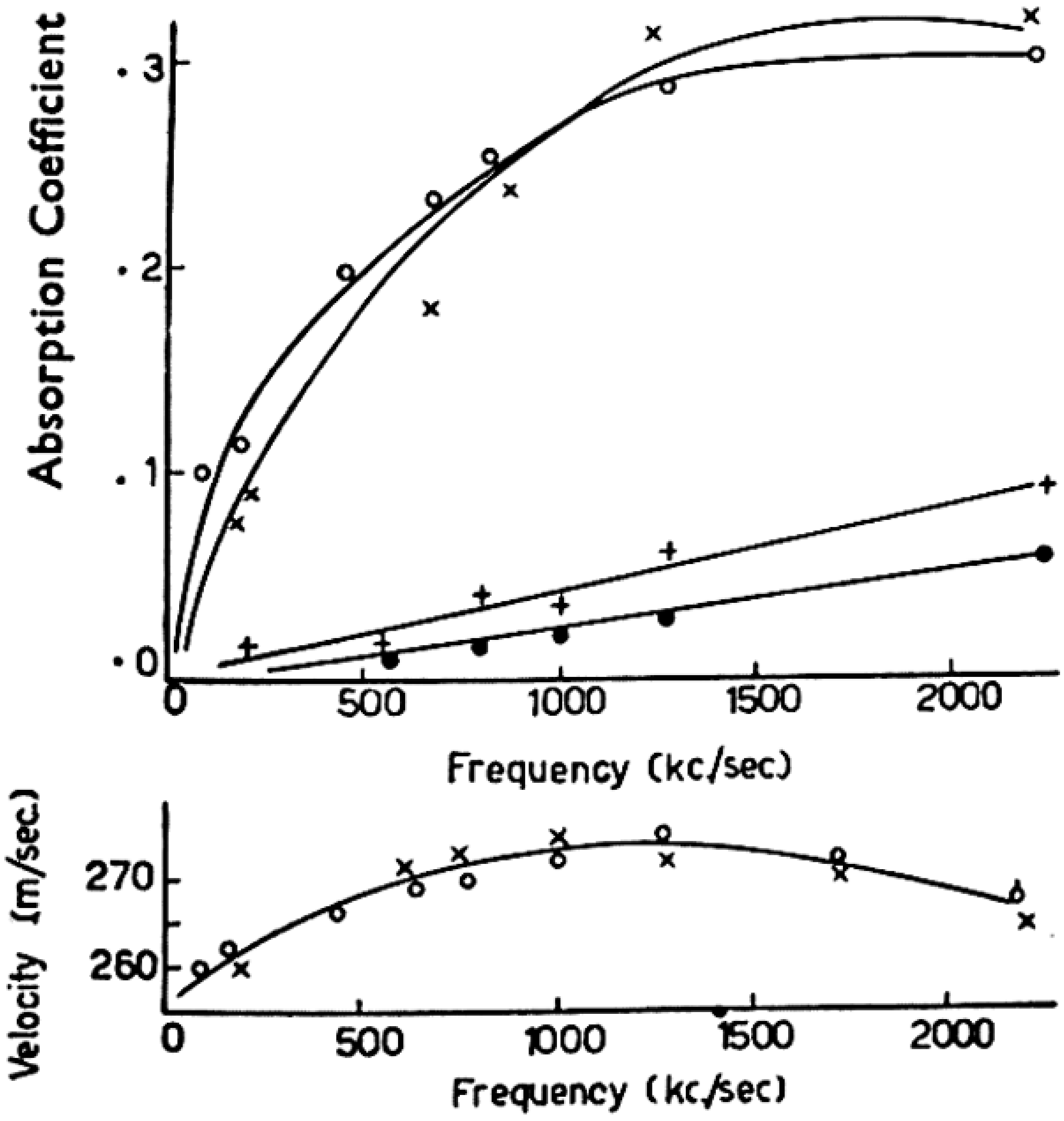

Fig. 41. Variation of Absorption Coefficient with Frequency in Four Gases; o carbon dioxide, × nitrous oxide, + oxygen, ● argon

Among other gases, ammonia has been found by STEIL[12] (*vide infra*) and OZDOGAN to show a small dispersion. It is less sure in chlorine and acetic acid vapour (STROTHER and RICHARDS[13]), in acetaldehyde (ALEXANDER and LAMBERT[14]) and hydrogen (ABELLO[9]; STEWART and HUBBARD[15]).

LEONARD[16] has described a method for measuring the absorption in a gas based on the system of GROSSMAN, in which a magneto-strictive source operates in a baffle and the intensity along the axis of the source is recorded by means of a microphone. The whole is mounted in a cylindrical chamber, of which the walls are covered with baffles to prevent reflected energy reaching the detector. Until this improvement was introduced the distance-intensity curves as the microphone was withdrawn showed "corrugations". The microphone was a "bender" built up from a bimorph element of Rochelle salt having a natural frequency of 45 kc/sec. To prevent reflections from its surface interfering with the source, it had a surface of only 3/8″ square. Work has begun in this apparatus on carbon dioxide, nitrous oxide, carbon disulphide, carbonyl sulphide and sulphur dioxide. For the linear molecules a linear relationship was found between the maximal absorption coefficient and the frequencies at which they occur. Great care was taken in the purification of the gases.

The method of PETERSON[17] developed further by its originator, of studying the propagation of ultrasonics in gases, using the diffraction of a monochromatic light beam has been applied by KELLER[18] to a determination of the absorption coefficients of argon, nitrogen, ammonia and carbon dioxide and their variation with pressure at a frequency of 4 Mc/sec. With the exception of argon, which conforms to theoretical prediction, the absorption is high compared with what would have been expected. PETERSON himself discusses the accuracy of measuring the ultrasonic intensity from the brightness of the diffraction pattern by photometry. He prefers to turn the axis of the sound beam slightly, relative to the optic axis, so that the angle between them is progressively lessened, taking photographs of the optical beam the while. Some inconsistencies in gases between intensities at different distances from the source are to be ascribed to the "electric wind" set up by a strongly vibrating source in a gas. This is a repulsion of the gas molecules by the quartz which tends to disturb the sound field (*cf.* p. 57).

At this point we may include some work by KNESER [19] on the absorption in nitric oxide, in spite of the fact that it was done with an audible source. He used OBERST's method (p. 105) in which the resonance curve of a cylindrical resonator (a brass tube 4.5 cm radius and 56 cm long) in a constant temperature bath is derived from the behaviour of a loud-speaker source at one end and a condenser microphone at the other. The spread of the resonance curve (and therefore the damping) was found to vary inversely as the square root of the absolute temperature — as would be expected on classical theory. KNESER was looking for deviations from this owing to electronic relaxation times.

Although nothing of this sort showed up within the limits of experimental error, it was possible to deduce an accurate value of the velocity in nitric oxide (in the range 300 to 5000 c/sec).

SCHMIDTMÜLLER [20] has used the same method, somewhat refined, for absorption, in nitrogen, oxygen, propane and carbon dioxide.

3. Propagation in Vapours

Apart from RICHARDS and REID [21], who claimed to have established dispersion of velocity in carbon disulphide, the principal measurements in vapours at ordinary temperature have been those of RAILSTON [22], JATKAR [23], MATTA [24] and RICHARDSON [25]. All have had trouble in their early attempts to use saturated vapours in the Pierce interferometer through condensation on the crystal eventually putting a stop to its vibrations. RAILSTON placed the reservoir of liquid in a small metal box attached to the side of the bath surrounding the container in such a way that heat reached it from one side only. This simple device ensured that the temperature of the liquid in the reservoir was always less than that in the container, when the bath heater was in use. The tube connecting the reservoir to the vapour container was lagged to prevent condensation in it. It was inclined for the greater part of its length, so that, in the unlikely event of condensation in it, the liquid would run back into the reservoir.

In the container itself, Fig. 42, the source *M* faced the reflector *R* on the end of the screw *F*, passing through the packed gland *G*. The latter was attached to a flat, ground, brass plate which was made to press a rubber gasket against the mouth of the container by tie rods *H*, *H* fixed to a metal base on which the vessel stood. The pressure on the gasket could be increased by turning thumbscrews on the rods. This method produced an airtight joint which could be made or broken in a few seconds. Vacuum grease was not used on the joint or in any other part of the apparatus since it was soon removed by the solvent vapours. To lubricate the taps a thin paste made of powdered graphite and sulphuric acid was first tried but the final choice was glycerine. This needed to be renewed at intervals, but was satisfactory in use. Throughout the apparatus no jointing material was used for rubber-glass junctions, only a little glycerine was smeared round the glass to make its separa-

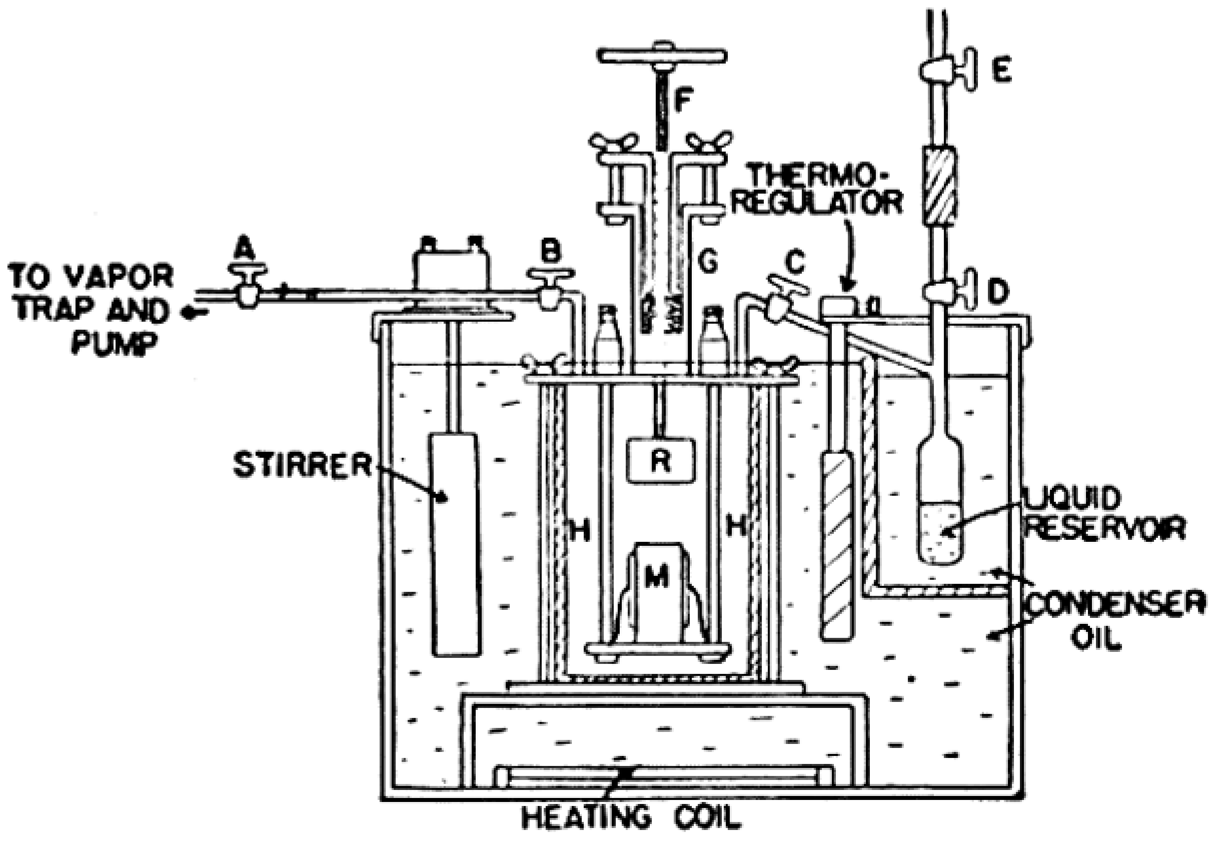

Fig. 42. Interferometer for Vapours (Railston)

tion from the rubber easier. Glass to rubber joints made in this way rarely leaked.

A stream of dry air was first passed through the apparatus. It was then evacuated and tested for leaks with a manometer. The oscillator was switched on and the liquid whose vapour was to be tested was admitted to the reservoir. A little air, which the pump could not remove, remained in the container. Its pressure was measured to enable a correction to be made to the velocity results for pressure deviations. The temperature in the oil bath surrounding the container had already been at the required value for an hour, having been set before the crystal oscillation was started. As an extra precaution to ensure that temperature equilibrium had been reached, the apparatus was left untouched for five to ten minutes longer. Then the temperatures of the container and reservoir were noted and the apparatus was ready for taking measurements.

It is necessary to correct the absorption results for diffraction (*cf.* p. 48).

JATKAR[23] has published a series of investigations on sound velocity in organic vapours, especially those used by RAILSTON, and has also deduced their specific heats. He used a small range of frequency from 49 to 129 kc/sec and a Pierce interferometer. He reported that the values of specific heats as calculated from the ultrasonic velocity in *iso*-propyl alcohol, *tert*-butyl alcohol and *n*-hexane differ from those calculated from spectroscopic data. This he considered as a sort of dispersion, or as he quoted "there is a partial disappearance of the share of rotational and deformation oscillation in the adiabatic cycle of the ultrasonic wave". For benzene he did not find any dispersion in this region. Furthermore, he did not measure the absorption of sound for any vapour.

An investigation of sound dispersion in acetaldehyde vapour was carried out in piezo-electric, magneto-strictive and Kundt's tube interferometers by ALEXANDER and LAMBERT[14] over a wide range of frequency in the audible and ultrasonic ranges under various pressures up to 4 atmospheres, while LAMBERT and RAWLINSON[14] covered a number of vapours in the ultrasonic range. Over the range $5.5 < \log f/p < 6.4$ the specific heat in benzene deduced from the velocity of sound falls by two fifths and in cyclohexane by nearly one-half; ethane shows a slight fall at the extreme of this range; acetaldehyde a rise of velocity between $\log f/p$ equal to 5 and 7. A number of other vapours showed an invariable velocity.

MOKHTAR and MATTA[24] working in the same field of vapours, but this time in the audible range of frequency, used a Kundt's tube adapted with a hot-wire detector, to suit the double purpose of measurement of velocity and of absorption of sound. They did not find any dispersion of sound in the vapours they used only higher values of absorption than those calculated from the classical theories.

MATTA and RICHARDSON[25] used a fixed-path hot-wire interferometer, similar to that already described (p. 110), to study V and a over a wide ultrasonic frequency range.

The results for vapours, both as to velocity and absorption constant are given in the tables at the end of the chapter (after RAILSTON and MATTA) with some velocity results of JATKAR (at two ultrasonic frequencies) and of MATTA and MOKHTAR (at sonic frequencies). Of the vapours studied, carbon disulphide, benzene and acetaldehyde show some dispersion of velocity, though none to the same extent as carbon dioxide and nitrous oxide. All show absorption greater than theory. RAILSTON remarks that in a number of vapours the absorption increases in approximate linear fashion with frequency.

4. Propagation in Moist Air

It has long been known from incidental observation that humidity affects the propagation of sound in air. Not only is there an increase in the velocity of sound waves, but apart from refraction owing to irregularities in the humidity, there is a change in the attenuation, so that distant sounds may often be heard more clearly under conditions of high humidity than when the air is dry. Similar effects of humidity on the absorption of sound in reverberation chambers were reported by SABINE [26], but it was left to KNUDSEN [27] to show that the absorption of sound in air as derived from reverberation experiments at audible frequencies reaches a maximum (as the humidity increases) at first and then falls, and that when the frequency is changed the position of the maximum also moves. This anomalous behaviour of sound in moist air was pursued into the ultrasonic range of frequencies by PIELEMEIER [28]. In 1937 he reported two humidity regions exhibiting abnormal velocity, within the range 50 - 100 kc/sec. Later he compared his measured velocities with those given by a formula of MILLER, based on outdoor experiments, which proposes a steady rise of velocity with humidity. Whereas earlier experiments had shown no measurable departure from the MILLER formula, PIELEMEIER attained values definitely higher at certain values of humidity and temperature.

Measurements of absorption in moist air in the ultrasonic region are scanty, and the methods employed open to criticism (*vide infra*). ROGERS [29] reported maxima of absorption at 45 % humidity in air (mixed also with carbon dioxide) at one frequency (410 kc/sec) while PIELEMEIER showed the existence of a critical vapour pressure (for maximum absorption) which was a function of the frequency, similar to that deduced by KNUDSEN for lower frequencies.

In 1938, MOKHTAR [30] and the author adapted the hot wire method previously described to air containing carefully measured quantities of water vapour.

The humid air to be experimented on was prepared in the desired state, passed into the acoustic interferometer, and its humidity measured on leaving. The air was first freed from carbon dioxide by passing it through potassium hydroxide and subsequently bubbling it through concentrated sulphuric acid. This was done because small concentrations of carbon dioxide are known to effect some dispersion, and it was not desirable to complicate the experiments by double dispersion. From the sulphuric acid bottle the gas could pass by alternative routes. One gave it further dryness by passing it over phosphorus pentoxide. The other led through aqueous solutions of salts whose saturation vapour pressure gave the air the approximate humidity desired.

The whole of this apparatus, as well as the interferometer, lay in enclosures which could be raised to any temperature up to 80 °C by means of external heating coils, and such portions of the connecting tubes as could not be accommodated in the chamber were heavily lagged with asbestos heated by coils to somewhat higher temperatures than the air passing through, to avoid risk of condensation.

After leaving the preparation chamber, the gas could pass directly through the hygrometer, for calibration purposes, or — when the ultrasonic measurements were being made — first through the interferometer and then through the hygrometer. This procedure was adopted as it was inconvenient to evacuate the interferometer before introducing the gas. The known vapour pressures over the solutions could, however, be used to calibrate the hygrometer since, when the interferometer was out of circuit, the remaining connections were completely airtight.

The hygrometer was also of the hot-wire type, in which the electrical resistance of a thin platinum wire fitted axially to a tube is used to measure the thermal conductivity of any gas in the tube. As the conductivity of air changes but slowly with the addition of water vapour, the single tube type of katharometer did not give sufficient sensitivity. Instead, four conductivity cells with associated hot wires were fitted up, two to contain moist and two dry air. These four wires were connected in a Wheatstone bridge so that each similar pair formed two conjugate arms of the bridge, thus doubling the sensitivity. The final design of the hygrometer is shown in Fig. 43. Each cell consists of a platinum wire, 0.001″ in diameter, mounted in a copper tube 1 cm dia-

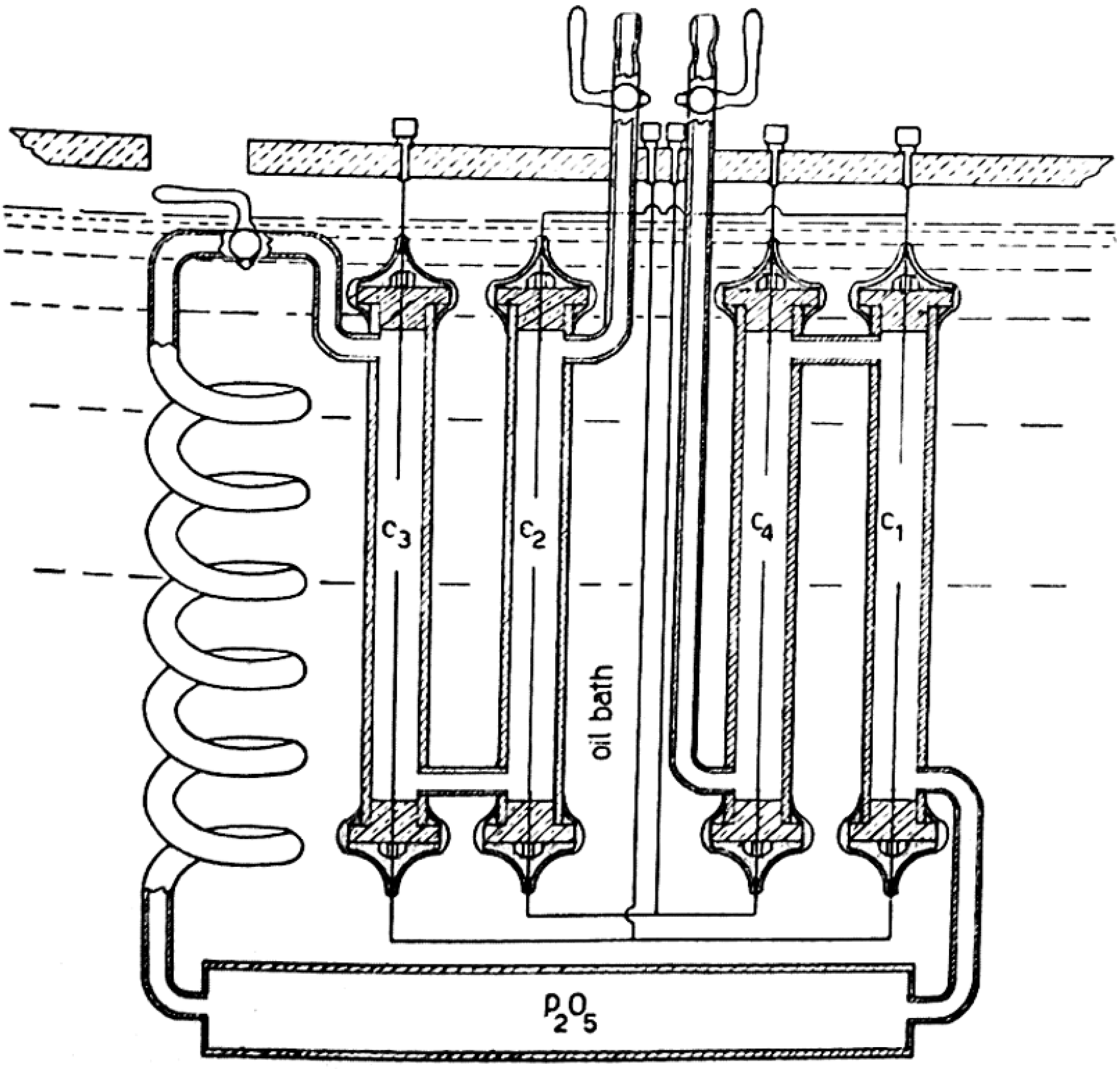

Fig. 43. Hot-Wire Hygrometer (Mokhtar and Richardson)

meter and 10 cm long. At its ends the wire is soldered to two thin brass rods, each brought through an ebonite cap and held under tension by nuts, sealed in position with sealing wax, and covered with a cement. The whole is mounted in a thermostat kept at 60 °C.

The humid air passes through two of the cells in succession, then through the phosphorus pentoxide tube and through the remaining pair of cells. The object of using the humid air, after drying it, as a standard gas is to make the readings independent of impurities other than water and

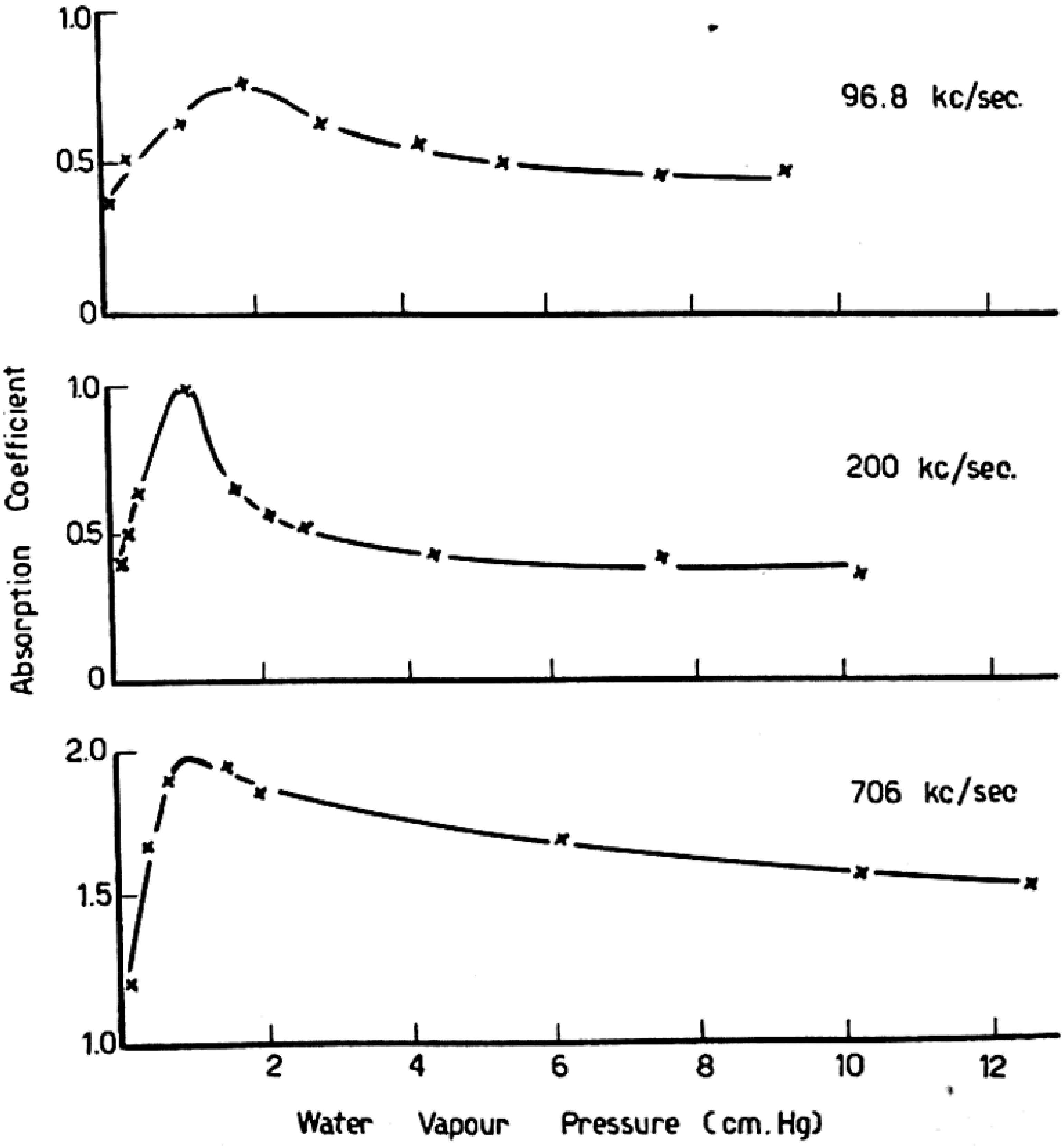

Fig. 44. Variation of Absorption Coefficient with Humidity of Air (Mokhtar and Richardson)

of casual changes of pressure and temperature in the hygrometer. It is, of course, very necessary in using such an apparatus to ensure that all four cells remain at the same temperature. The calibration curve was obtained in the form of the positions of the galvanometer lead on a slide wire placed between two of the arms of a Wheatstone bridge for a series of known vapour pressures over the aqueous solution employed.

Again we observe enhanced values of the absorption constant, with a tendency of α/f^2 to decrease over this range, as the frequency goes up. Whereas in the audible region the maximum value of α moves up the scale of water-vapour content, it retreats little as the frequency goes up in the ultrasonic gamut (Fig. 44). The maximum V_0 protrudes less to the general level appropriate to a given humidity, as the frequency rises.

5. Propagation in Other Mixtures of Gases

Since his first experiments with air-water mixtures, KNUDSEN has extended his reverberation chamber measurements to air and oxygen with other admixtures. For example, in conjunction with KNESER[31] he has put a number of organic and inorganic gases in small quantities into oxygen, and they all increase the audio absorption coefficients.

With the exception of water most of the impurities cause an upward shift Δf of the frequency for maximum absorption in direct proportion to the concentration C of the adjunct. Thus

$$\Delta f = aC$$

but for water

$$\Delta f = aC + bC^2,$$

where a and b are constants. The value of a varies greatly between different gases, and seems to be characteristic of the molecular structure, though its precise significance remains to be discovered. Some relative values of a are given in a table: — the gas with which the mixture is made is oxygen in every case.

Impurity	Relative values of a
Ethyl alcohol	60
Ammonia	16
Benzene	13
Ethylene	4
Carbon tetrachloride	1

The diatomic gases and carbon dioxide as adulterants showed a value of a less than 1. Although shift of the absorption peak is comparatively easy to observe, the recorded effects on velocity are small, and, one would imagine, difficult to precise. For example, KNUDSEN and OBERT [32] have readily detected the shift of the peak absorption frequency in oxygen with a percentage of added water vapour or ammonia up to 3.5 kc/sec, whereas RICHARDS [33] has to look for a change of less than 1 per cent in the velocity in ethylene, when small quantities of deuterium are added. The effect of impurity on absorption is in fact well established in the case of oxygen at sonic frequencies with added water or ammonia.

The other interesting mixtures concern carbon dioxide. EUCKEN and BECKER [34] found that the rise in velocity — which as we have noted, occurs at 100 kc/sec in the pure gas — is gradually pushed up the frequency scale by small quantities of indifferent gas, *e.g.* to 10^6/sec at 12% impurity.

PIELEMEIER, SAXTON and TELFAIR [35] have measured the absorption in air and its constituents when adulterated with carbon dioxide. Other mixtures have been studied at temperatures below normal, particularly by the Louvain school: mixtures of the hydrogen, oxygen and the rare gases. This work is referred to again later.

It should be noted that in none of these cases is a chemical reaction concerned. However RICHARDS and REID [36] have studied the dissociation of nitrogen tetroxide in the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ by ultrasonic methods in the hope of being able to sort out the effect we have been discussing from a purely chemical one. Both these lead to the same ultrasonic effects, *viz.*, increase of velocity and absorption, the latter appearing as a change of phase between pressure and condensation. These writers, contrary to TEETER [37], think that it should be possible, at least in gases for which the heat of dissociation is large, to disentangle the two effects particularly if the readings in the dispersion range be made at various pressures and temperatures.

6. Effects of Pressure and Temperature

According to classical theory, the velocity of sound does not change with pressure but increases in proportion to the square root of the absolute temperature. (These assumptions are in fact used in "reducing" a measured velocity to that proper to N.T.P.). The absorption on the other hand, decreases as the pressure goes up, for in equation (24), p. 52, the kinematic viscosity ν decreases directly with specific volume insofar as η itself is independent of pressure. (This is true for gases, except at very low pressures). Again the early measurements of velocity were made at audio-frequencies, notably by KOCK on air between 1 and 200 atmospheres and by SPAKOWSKI [38] on carbon dioxide between 1 and 85 atmospheres. RICHARDS and REID [21] first published in 1934 a few velocity results

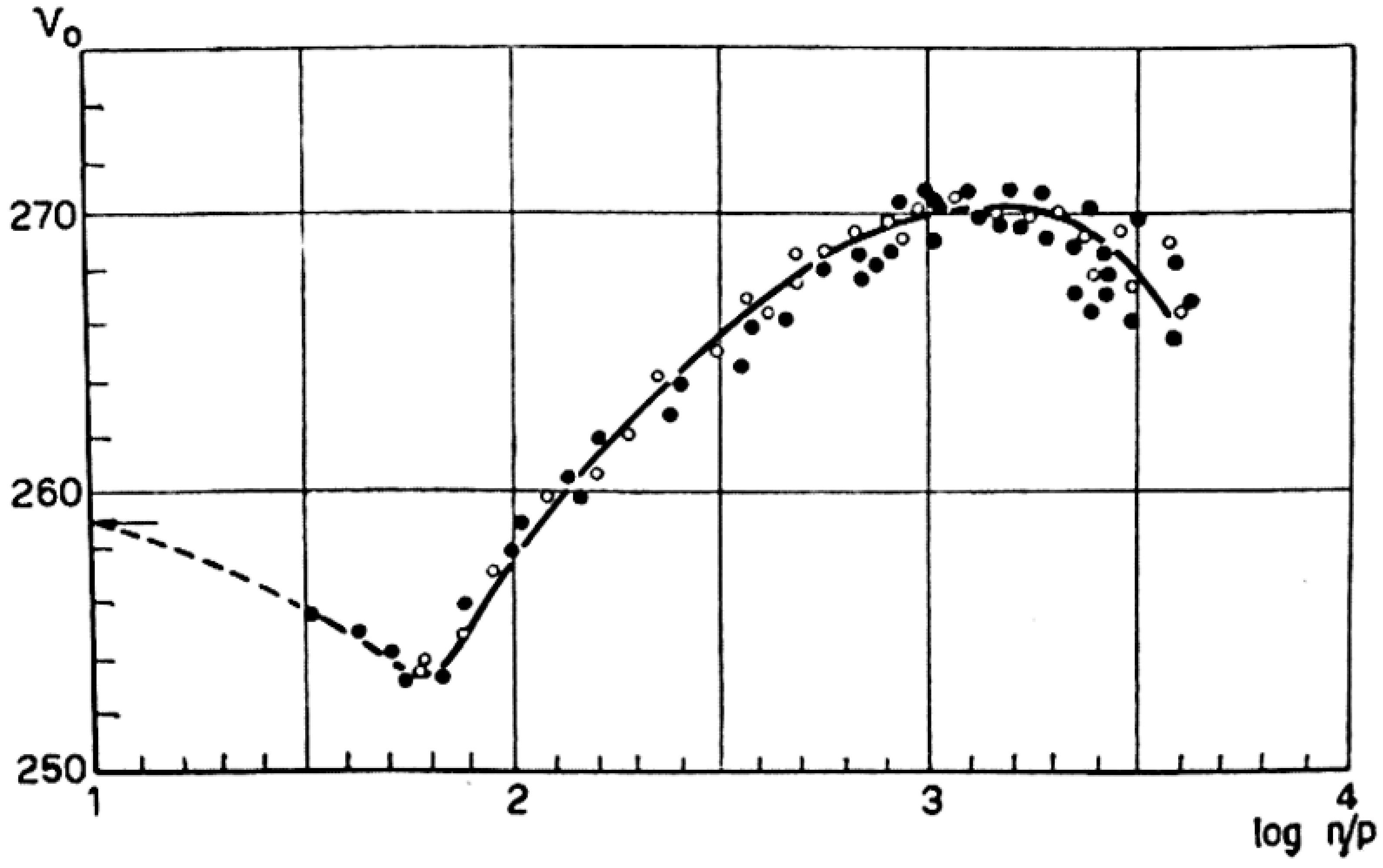

Fig. 45. Dispersion of Velocity with Frequency/Pressure in Carbon Dioxide (RAILSTON and RICHARDSON)

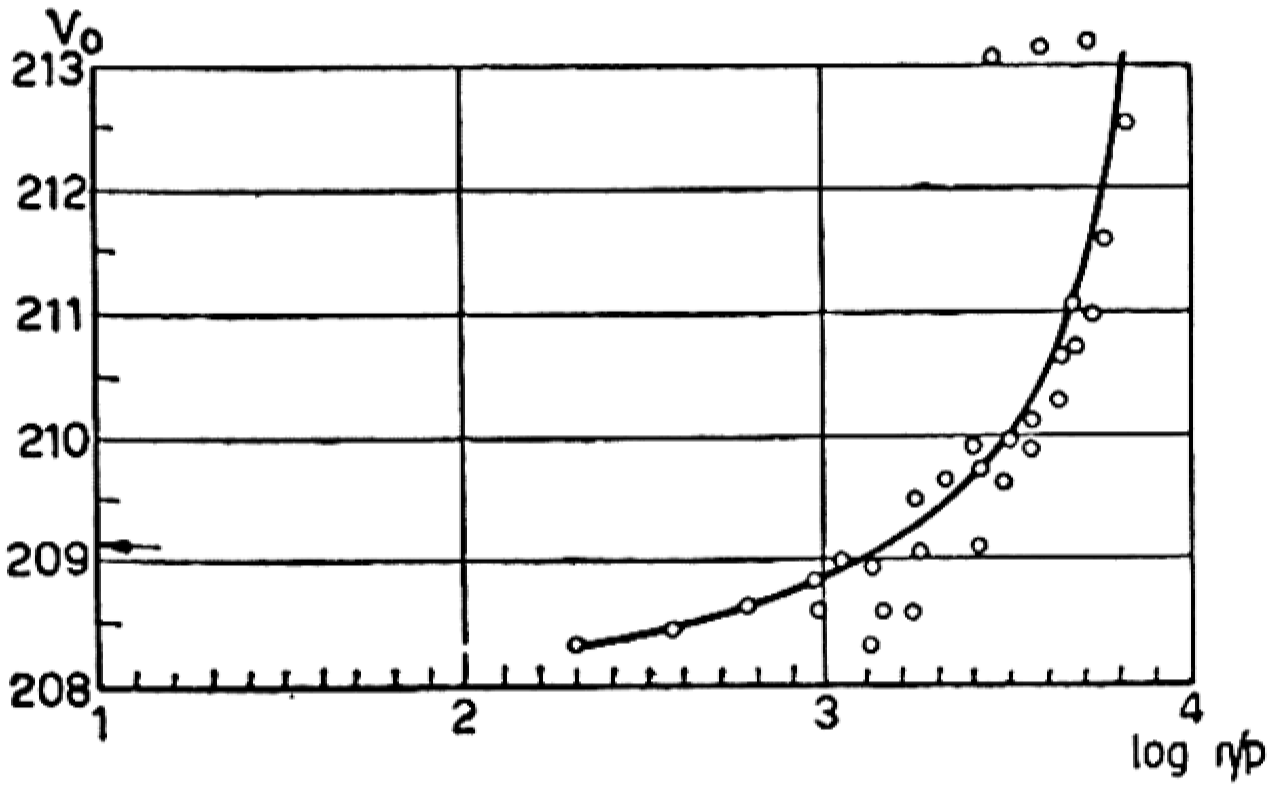

Fig. 46. Dispersion of Velocity with Frequency/Pressure in Sulphur Dioxide

in carbon dioxide at 94 atm. and 450 kc/sec. Railston and the author [39] in the following year published an extensive series of measurements of both *V* and *α* in this gas, nitrous oxide and sulphur dioxide at a number of frequencies between 40 and 1800 kc/sec, and pressures lying between 10 and 150 cm of mercury. The velocities — "reduced" to 0 °C — were found to combine well into a single curve when plotted against the parameter f/p (see Figs. 45, 46). In fact, the curves so obtained resemble those already noted for atmospheric pressure.

The dispersion is apparent as a rise of velocity in the neighbourhood of $f/p = 100$, with a more gradual fall on each side. In sulphur dioxide (Fig. 46) this effect is only beginning to occur at the maximum values of f/p attained. (The arrows on these two figures indicate the value of *V* at low frequencies.) Finally on Fig. 47 we have the absorption coefficient plotted against pressure at four frequencies. In each case the absorption rises as the frequency is increased or the pressure reduced, but plotting against

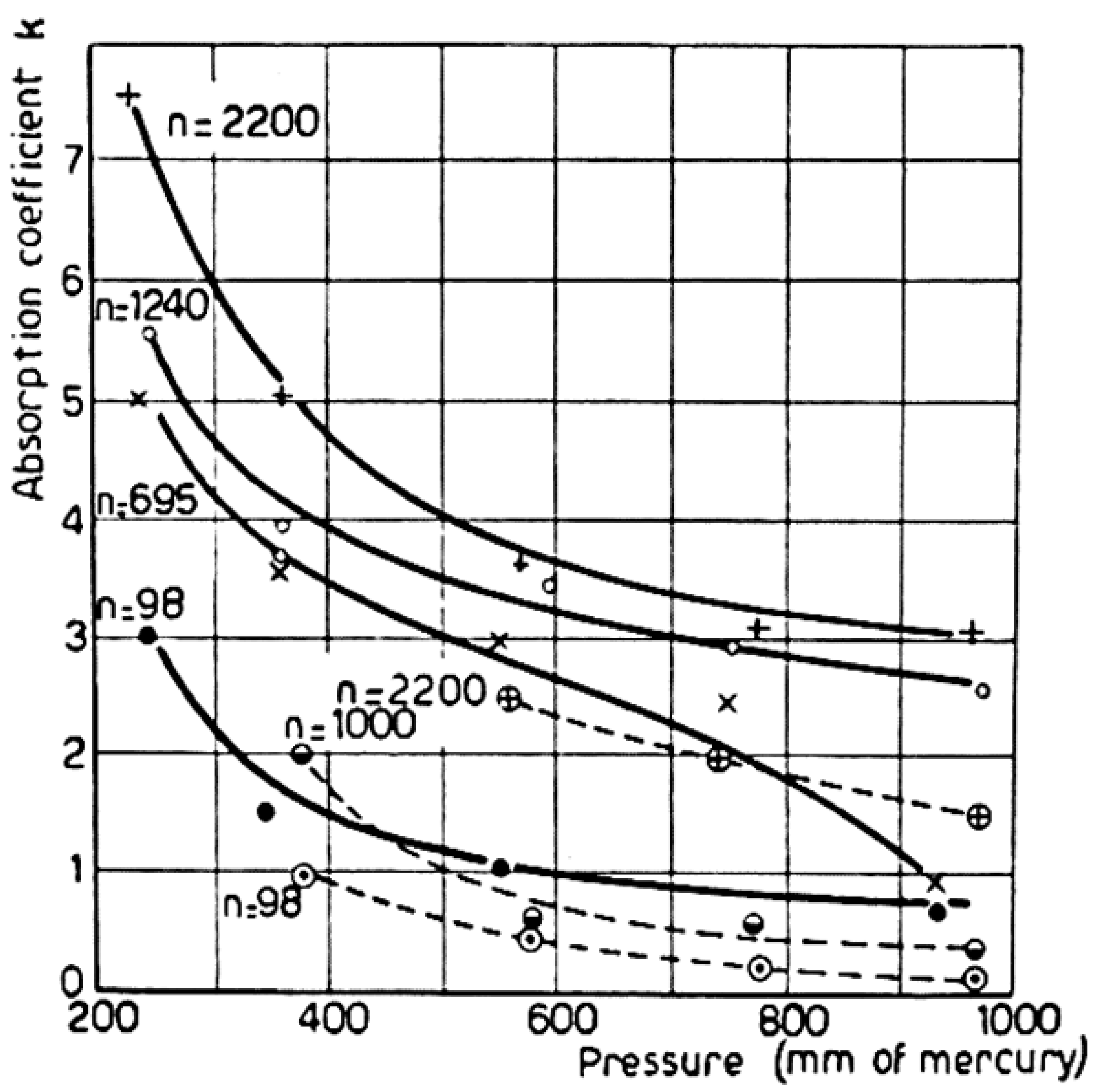

Fig. 47. Variation of Absorption Coefficient with Pressure in Three Gases (*n* in kc/sec)

f/*p* does not reduce the results to a single curve so successfully as it did in the case of the velocities. It must be remembered however that α cannot be determined with the same accuracy as V by a hot-wire method or indeed by any other method. In the table which follows are shown the values of $\alpha\lambda^2$ which from equation (27) should be inversely as pressure.

Pressure (mm mercury)	200	360	560	760	1000
$\alpha/\lambda^2 \cdot 10^5$ (carbon dioxide)	7.5	4.0	2.7	2.0	1.5
$\alpha/\lambda^2 \cdot 10^5$ (sulphur dioxide)	5.5	3.7	2.4	1.5	1.1

PUMPER [40], on the other hand, who worked with air and carbon dioxide at pressures down to one tenth of an atmosphere found a steady rise in velocity in both gases (at a single frequency of 443 kc/sec).

In another research RICHARDS and REID[41] tested ethylene at three frequencies, f/p going from 10 to 10^4 while V_0 rose 6 per cent.

STEIL[12], as already noted, found a small dispersion in ammonia gas, which he followed through a range of pressure (see Fig. 48).

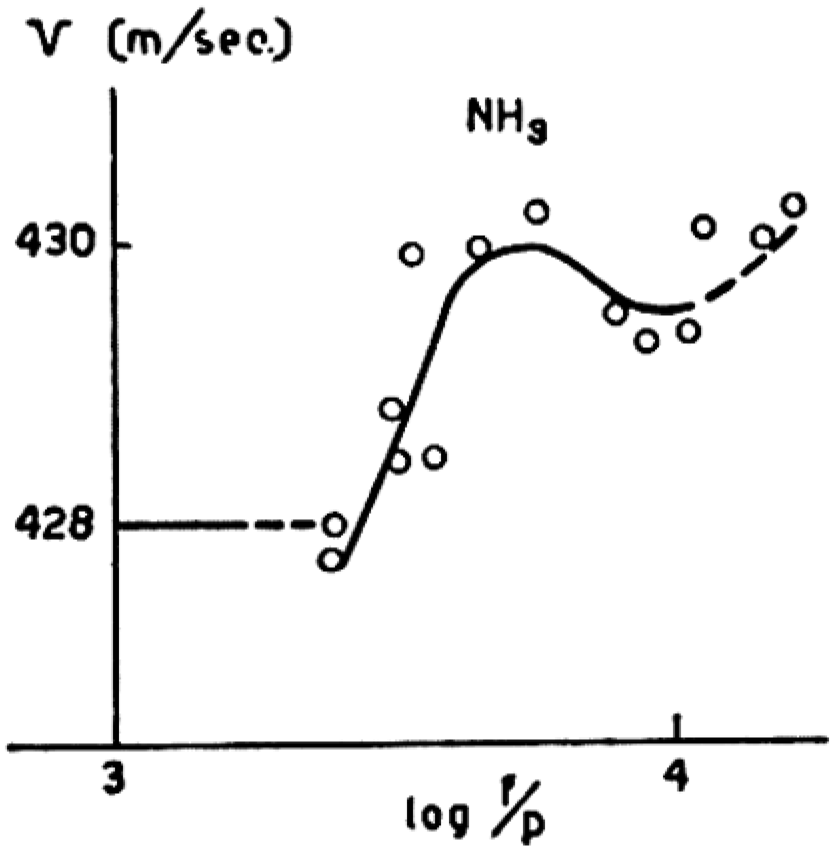

Fig. 48. Dispersion of Velocity with Frequency/Pressure in Ammonia Gas (STEIL)

In hydrogen ZARTMAN[42] finds that the velocity remains constant until either the frequency is very high or the pressure low.

ABBEY and BARLOW[43] measured the velocity in a tube at audio-frequencies and very low pressures, down to 2.5 cm mercury, in carbon dioxide, oxygen, and nitrogen. They used a loud-speaker as source and tuned it until the "feed-back" acting on its driving circuit indicated that the gas column vibrated in resonance. After applying the

Kirchhoff tube correction (to a 3″ diameter tube) they obtained velocities which steadily rose by 1 or 2 m/sec, between atmospheric pressure and the rarest gas in which it was possible to propagate sound.

Leaving aside for a moment the further discussion of results at high pressures, let us turn to experiments in which the temperature is raised above the normal.

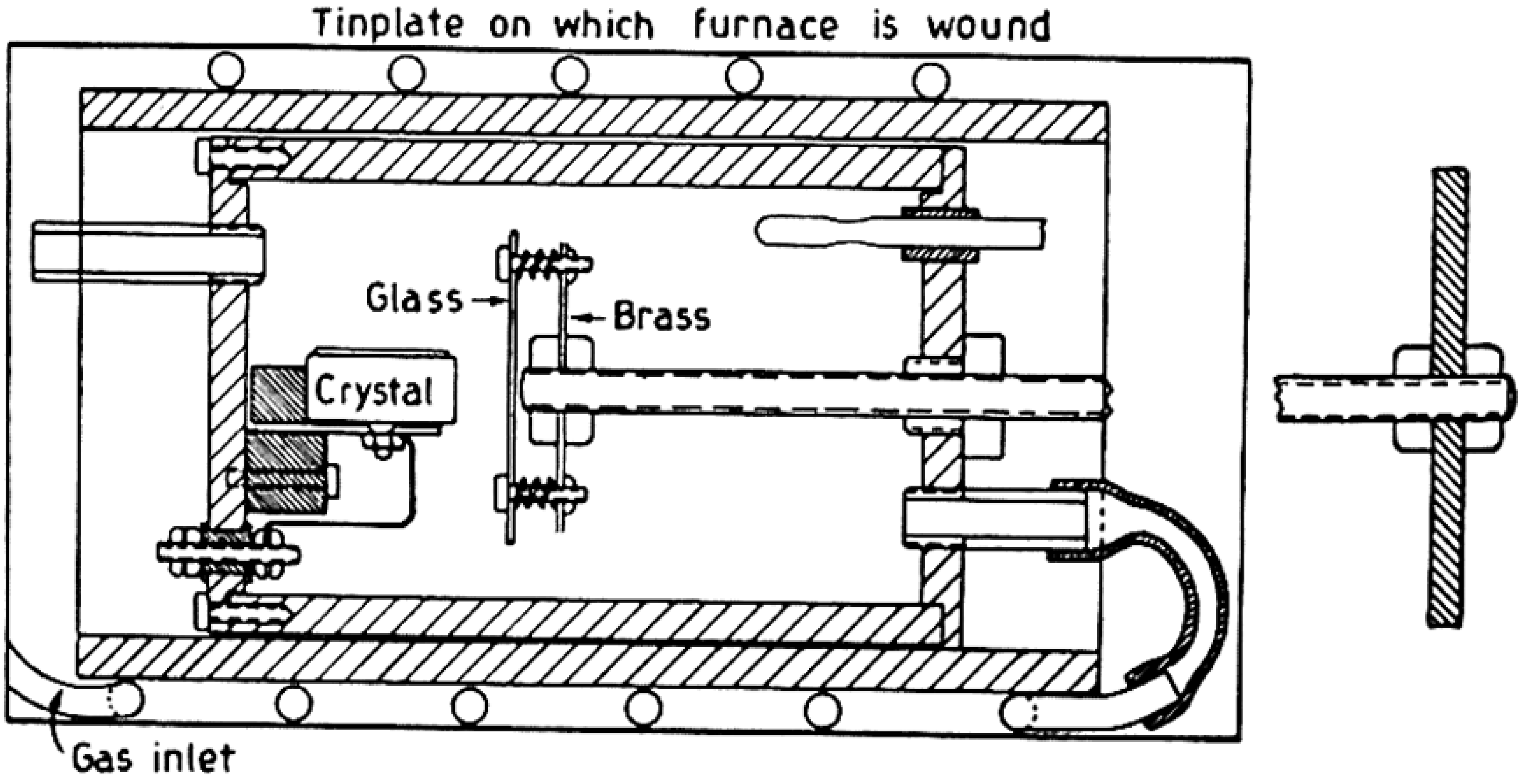

Fig. 49. Interferometer for Temperature Effects (Penman)

Fig. 49 after Penman [44] is a typical ultrasonic interferometer for this type of work. The inner tube is of iron, 5½″ long and 2½″ in diameter. One end is permanently closed and carries a thermometer, a gas tap, and a long brass screw on which the reflector is mounted. The other end is detachable and on it is mounted the crystal-holder, while through it pass a gas tap and two insulated terminals by means of which connection is made to the crystal electrodes. This end is bolted on to the tube, a rubber gasket ensuring a gas-tight fit.

References pp. 155–157

A glass plate is used as a reflecting surface and is mounted upon a brass frame with levelling-screws and springs. This brass frame is carried on the end of a screw of pitch 1 mm, the other end of which carries a circular scale by means of which the traverse of the reflector is measured. With this arrangement it is possible to ensure that the reflecting surface shall be perpendicular to the screw and thus remain parallel to the vibrating surface of the crystal as the screw is turned.

The experimental tube telescopes into a second iron tube of greater length round which several turns of ¼-in copper tubing are wound. Over this is wrapped an enveloping sheet of tinplate, providing a core upon which the wire of an electric furnace is wound. The copper tubing is connected at one end to the gas supply and at the other to the tap at the fixed end of the experimental tube. While observations were in progress a slow flow of gas was maintained through the coil, the gas becoming heated in the process and being then passed through the interferometer tube. The temperature of the gas in the latter was read at the same time. This arrangement maintained a small pressure-gradient from the experimental tube outwards, so preventing a possible leakage of air inwards.

PENMAN's [44] velocity results in carbon dioxide are shown on Fig. 50 together with some results of RICHARDS and REID at an intermediate frequency. All these are "reduced" velocities. Although these obviously trace the usual dispersion curve in a reverse direction, it is not so simple as

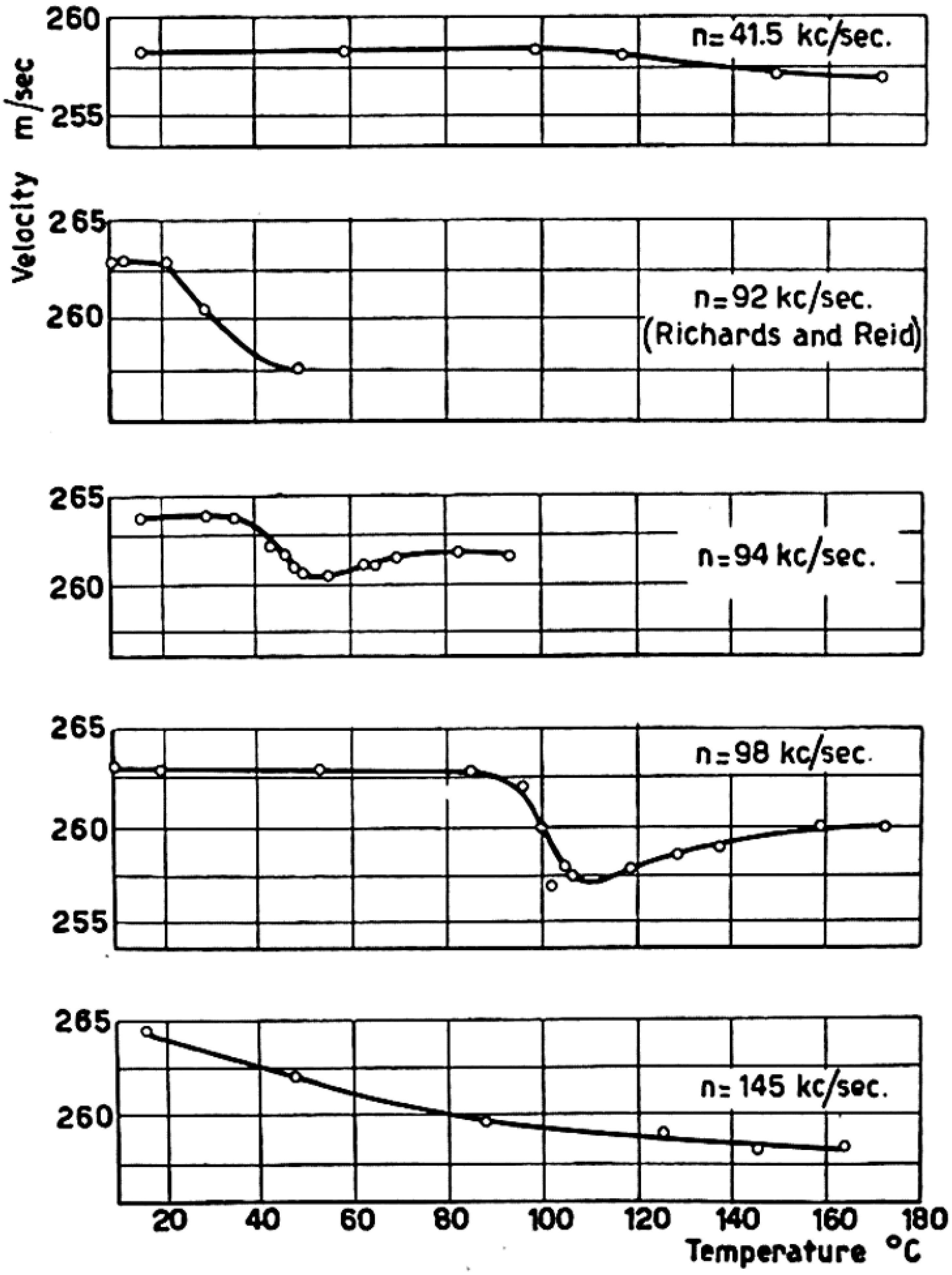

Fig. 50. Dispersion of Velocity with Temperature in Carbon Dioxide (PENMAN)

in the corresponding pressure variation to combine them on the basis of a single parameter of frequency and temperature. The best one can do is to take the temperature corresponding to the middle of the downcast at 262 m/sec and plot this against temperature, when one obtains a straight line (Fig. 51). The velocity in sulphur dioxide is nearly constant within this temperature range (18° to 180 °C).

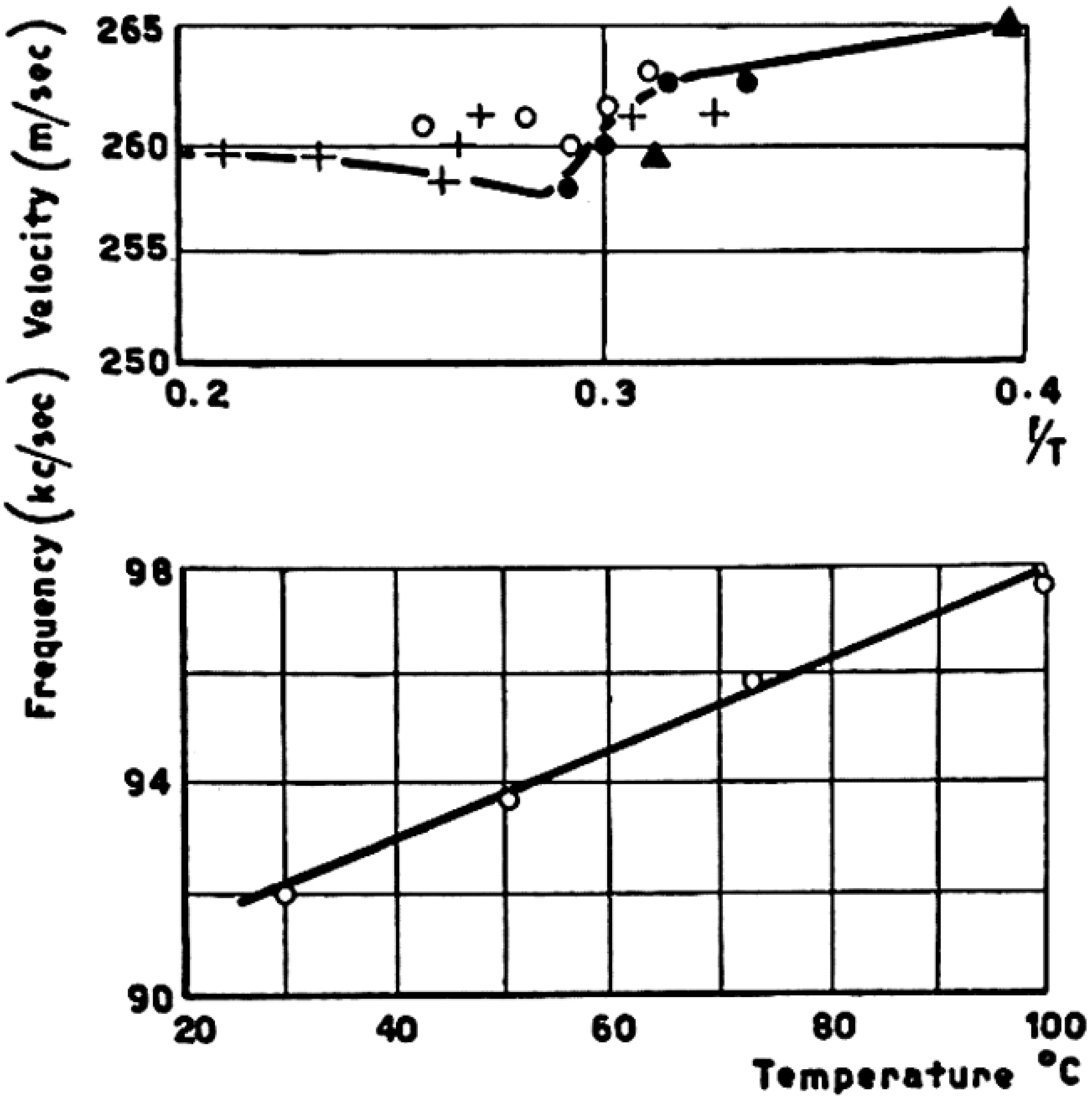

Fig. 51. Temperature of Maximum Dispersion in Carbon Dioxide as Function of Frequency

These results were confirmed by WARNER [45], as to the general shape of the curves.

OVERBECK and KENDALL [46] made measurements in pure carbon dioxide gas at temperatures ranging from 25° to 530 °C and frequencies from 27 to 147 kc/sec. These authors confirm that the velocity (adjusted to 0 °C) falls as temperature increases, but, contrary to results by PENMAN [44] and by WARNER [45], their work suggests a much more gradual fall. The difference is ascribed to impurities and temperature gradients in the earlier work. It should be pointed out that their room temperature value of the reduced velocity is considerably above the accepted audible value, though their frequency was only 90 kc/sec.

EUCKEN and NUMANN [47] report results at a single frequency 200 kc/sec in CO_2 and N_2O. They measured α as well as V.

In another paper, RICHARDS and REID [41] find that the velocity in ethylene rises in proportion to the absolute temperature.

BENDER [48] used a single quartz operating each way against a pair of reflectors, one each side of the quartz. If a is an apparatus constant to represent errors due to spreading of the radiation *etc.*, and if one reflector is set at a distance l_1, corresponding to n_1 half wave-lengths and the other at l_2 corresponding to n_2 half wave-lengths, we have

$$l_1 = a + n_1 \lambda/2$$

$$l_2 = a + n_2 \lambda/2$$

so that $l_1 - l_2$ is occupied by $n_1 - n_2$ half wave-lengths. BENDER then kept the reflectors fixed and raised the temperature until another integral number of (new) half wave-lengths intervened. In this way he got values (V) for velocity in nitrogen, carbon monoxide and nitric oxide at 1500 kc/sec. On plotting $V/T^{\frac{1}{2}}$ against T (temperature) he obtained a curve which rose to a maximum and then fell. This dispersion region should move to higher temperatures as the frequency is raised, according to BENDER, though actually he used only the one frequency in his research.

7. Propagation at High Temperatures and Pressures

SHERRATT and GRIFFITHS [49] made velocity measurements in carbon monoxide over an extensive temperature range of 1000 °C to 1800 °C, but at two frequencies (about 30 and 8 kc/sec) only, scarcely enough to establish a dispersion of velocity. As the upper limit of temperature at which quartz will exhibit the piezo-electric effect is about 500 °C (p. 28), it was necessary to have the source in a cooler atmosphere than the gas. The latter was contained in a carbon tube, ½″ diameter and 3′ long mounted on two electrode blocks of aluminium and contained in a wider iron tube, thermally insulated. The reflector was a graphite rod enlarged at one end to form a piston (Fig. 52). A current passing between the aluminium blocks heated the tube. Below this was the cooling coil and the crystal source, which could be shifted to two alternative positions, one under the experimental tube and one over a side tube containing carbon monoxide at room temperature. Corrections for the effect of the tube on the velocity and for expansion of the graphite rod were applied. The ratio of specific heats was found to run from 1.329 to 1.371 at the lower frequency and 1.309 to 1.360 at the upper frequency over their temperature range.

HODGE and HUBBARD [50] have extended the earlier measurements on the change of ultrasonic velocity with pressure up to 100 atm. using a Pierce interferometer and five frequencies from 88 to 500 kc/sec. The chamber was constructed out of a block of steel with a cap which could be

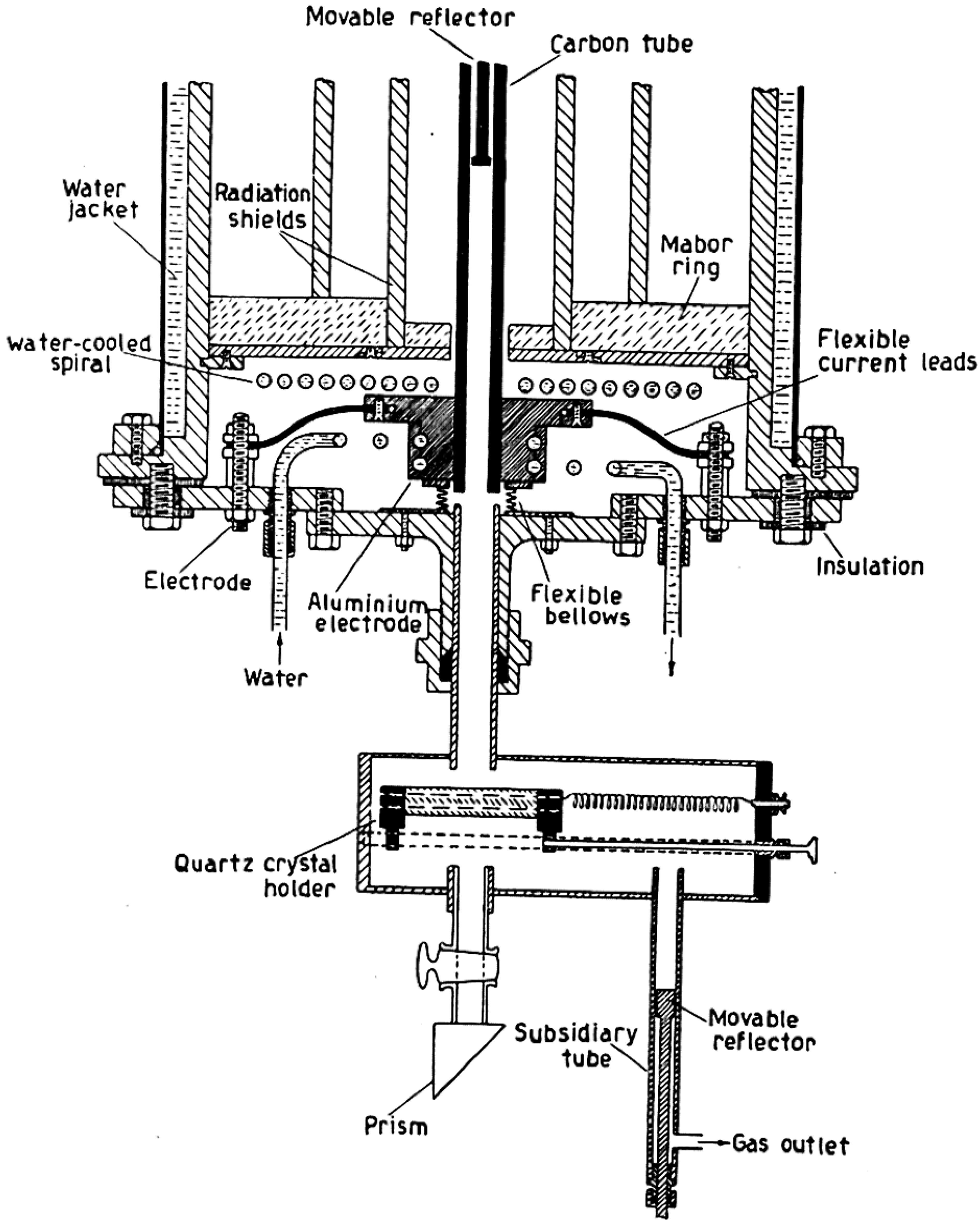

Fig. 52.
Interferometer for High Temperatures (Sherratt and Griffiths)

removed to replace the quartz oscillator. The metal to metal joint which permitted the apparatus to be sealed was made by cutting a circular V-shaped ring into a soft copper gasket with sufficient force to cause the copper to flow. The force

References pp. 155–157

to do this was applied by screwing down two bolts with a wrench, making a gas tight seal even at 100 atm. The pressure was measured on a Bourdon gauge. For the results, a steady rise was observed in hydrogen, helium, oxygen and nitrogen, but a fall with increasing pressure was apparent in carbon dioxide. No evidence of the usual S-shaped curve, observed in the case of carbon dioxide by earlier workers, appears in the results but this is possibly because pressures below atmospheric were not applied. In conjunction with known values of compressibility, the ratio of specific heats for these gases at various pressures is then deduced.

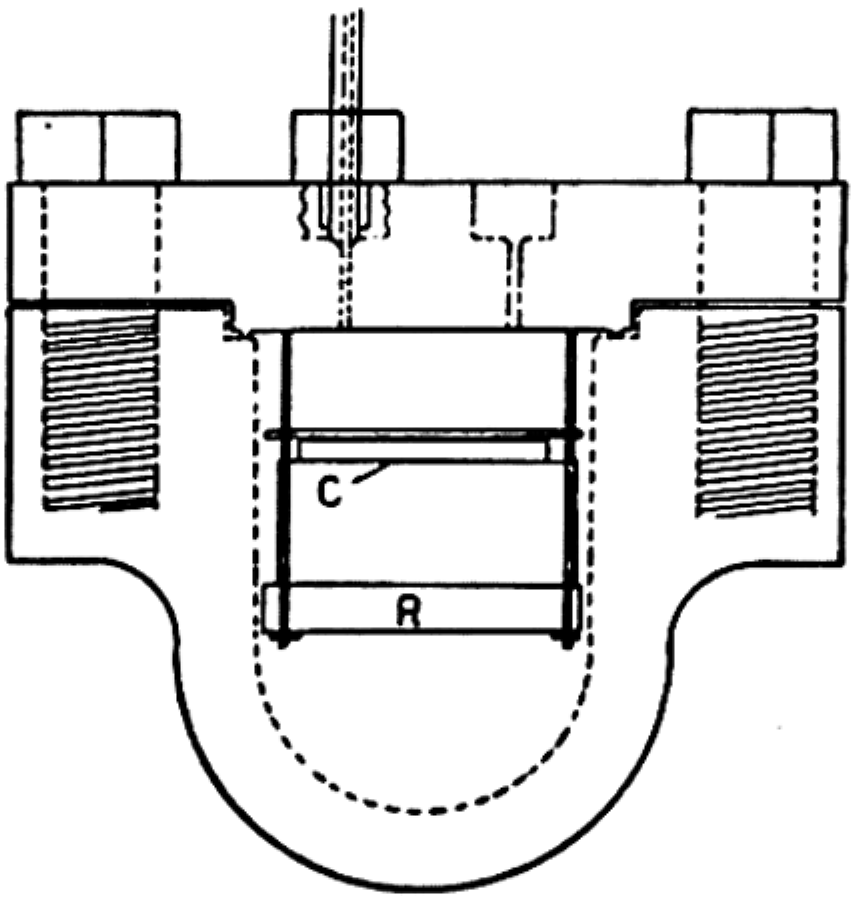

Fig. 53. Interformeter (Fixed Path) for High Pressures (Herget)

Herget[51] has designed an ultrasonic interferometer (Fig. 53) in which the quartz (*C*) and reflector (*R*) are kept at a fixed distance, and in which a gas may be put under pressure. This type of instrument possesses advantages over the more usual one in which the reflector is moved and the half wave-length estimated from the recurrence of peaks in the driving current, for when gases under pressure are in question it eliminates the gland and the possibility of leaks through it, where the reflector guide enters the chamber. As the frequency of the oscillator is fixed as well as the path length, it is then necessary to alter the pressure until this path becomes equal to an integral number of half wave-lengths, as shown by the variations in the current through the driving circuit. The value of the velocity of sound is supposed known at some pressure within the range at which the gas is first introduced. The gas is then allowed to leak out slowly through a tap and the number of peaks passed as the pressure is reduced is counted. To test the instrument the velocity in ethylene was measured both in it and in one in which the reflector moved, namely, the variable path type of instrument. The two sets of data concur within one-half per cent.

Into this interferometer HERGET has introduced carbon dioxide to 100 atmospheres, and subsequently ethylene to 75 atmospheres and several temperatures. He found that the velocity at a constant temperature gradually fell to a minimum just below the critical pressure and thereafter rose steeply. Difficulties in the maintenance of the crystal vibrations were encountered in the neighbourhood of the critical point, particularly in ethylene. Only one crystal (frequency 266 kc/sec) was used.

PARBROOK and the author [52] have extended these measurements using a range of frequencies in carbon dioxide, in an endeavour to study the behaviour of the noted dispersion at high frequencies and beyond the critical point.

A variable-path interferometer was built in a bomb capable of withstanding 200 atm. pressure. The reflector, accurately aligned, was moved by an electric motor from outside the vessel, and the reaction on the quartz, noted in the anode current, shown on a photographically recording galvanometer as the reflector moved. Measurements of V and α in carbon dioxide (critical temperature 31 °C, and pressure 77 atm.) using several frequencies between 200 and 700 kc/sec were made; also in ethylene (critical temperature 10 °C and pressure 48 atm.) at one frequency. At these pressures, dispersion of the velocity in carbon dioxide has disappeared (at any rate, over the range of present-day attainable frequencies), but the velocity curves show a sharp reversal of the trend of variation with pressure at the critical point (Fig. 54). Though the absorption coefficient falls with increase of pressure, it becomes nearly steady

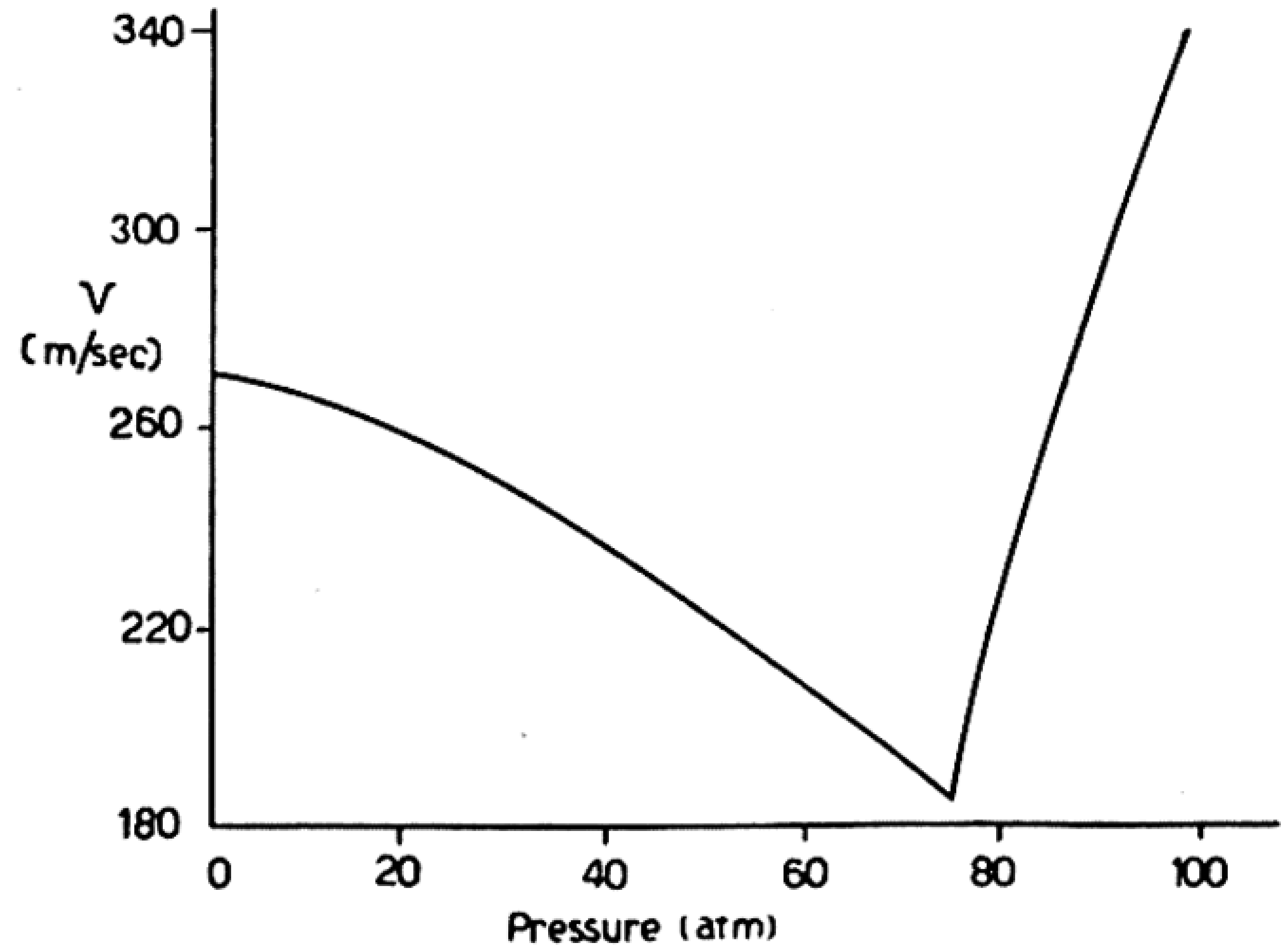

Fig. 54. Velocity in Carbon Dioxide near Critical Point

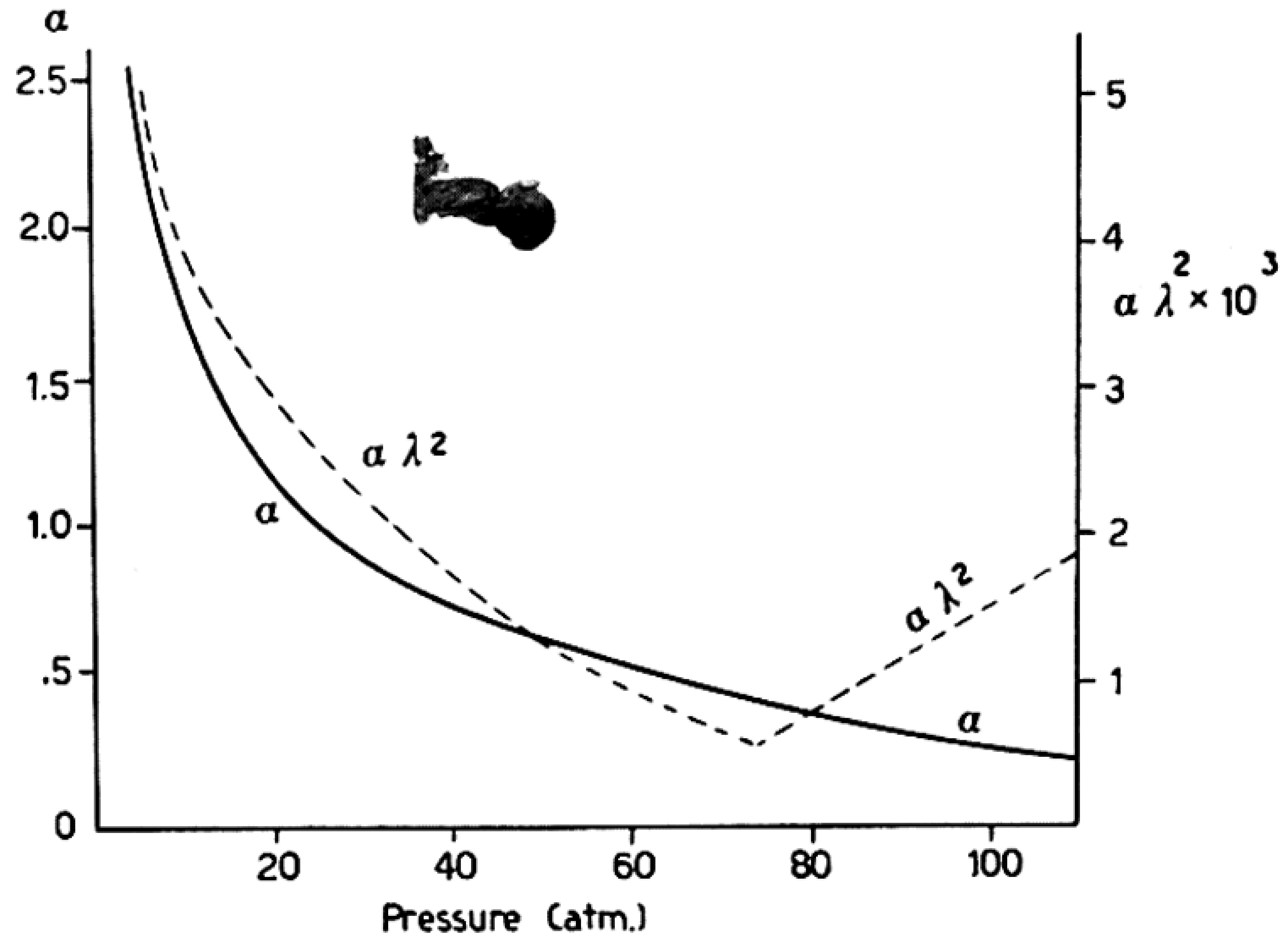

Fig. 55. Absorption in Carbon Dioxide near Critical Point (PARBROOK and RICHARDSON)

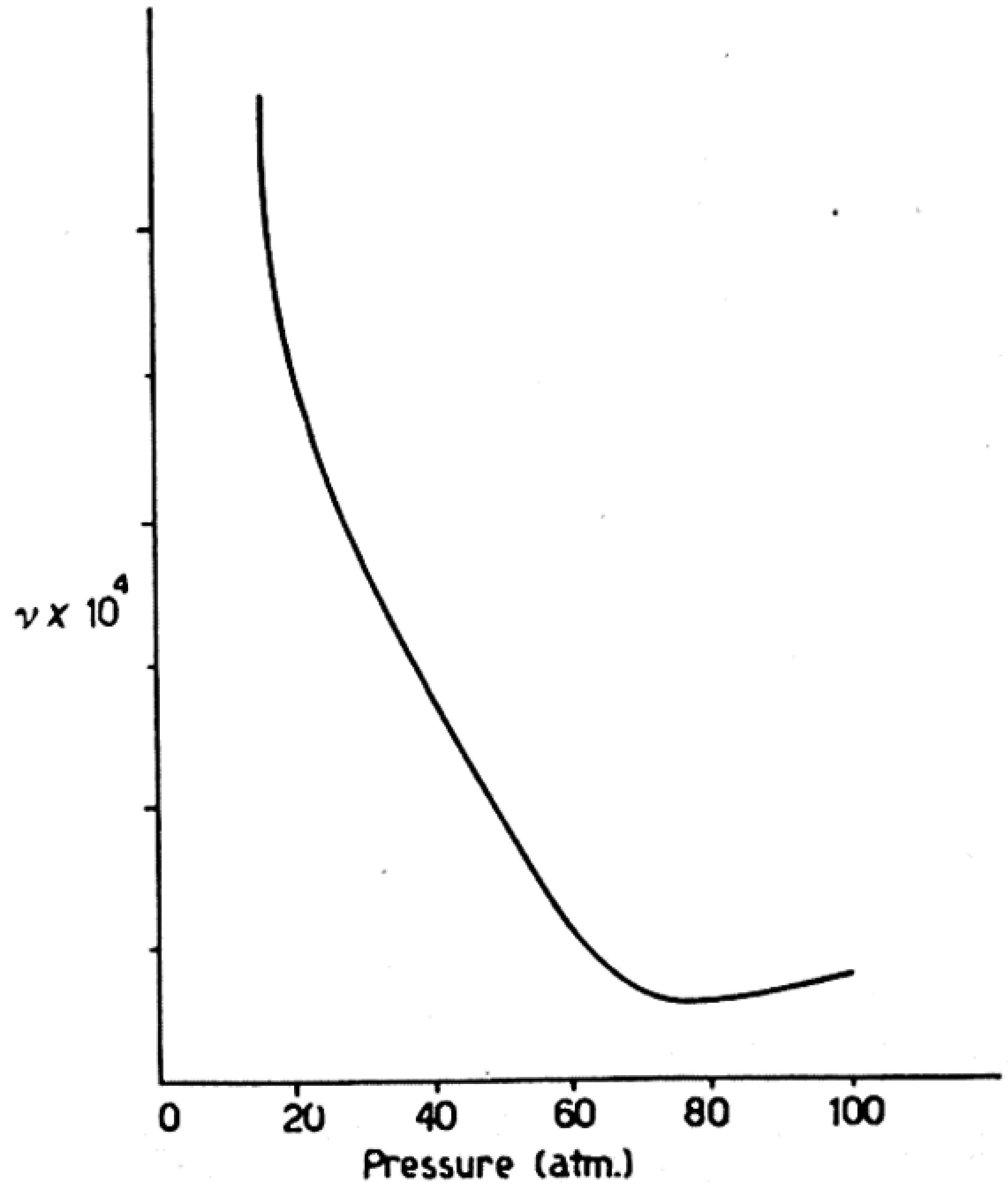

Fig. 56. Viscosity of Carbon Dioxide near Critical Point (PHILLIPS)

beyond the critical pressure. If $\alpha\lambda^2$ be plotted as a criterion of ultrasonic viscosity (*cf.* eqn. (27) p. 106 and ignoring the small change in V) there is again a discontinuity at the critical point (Fig. 55) where, indeed, the absorption often rises to a high and uncertain peak (not shown in the figure).

This parallels the trend of viscosity with pressure in *steady* flow as revealed in the measurements of PHILLIPS (Fig. 56) though the absolute values of ultrasonic viscosity are much higher. These experiments are still in progress.

8. Effects at Low Temperature

The fixed path interferometer with a 600 kc/sec quartz has also been used in HUBBARD's laboratory on "pure" air and methane from 0°C down to 90 °K*. In both gases, the variation of velocity was linear with temperature over this range.

A great deal of work has been done by VAN ITTERBEEK [53] and his students at low temperatures. Their variable-path interferometer is formed in a pyrex flask surrounded by the refrigerating liquid (Fig. 57). The gas is pumped in at atmospheric pressure. When it is desired to measure the pressure-dependency of V, the pressure is lowered by letting some of the gas stream out into an evacuated flask of large capacity.

In nearly all the pure gases — which were mostly constituents of the atmosphere — the velocity: pressure curves

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* indicates absolute temperature, *i.e.* on a Centigrade scale with zero at —273 °C.

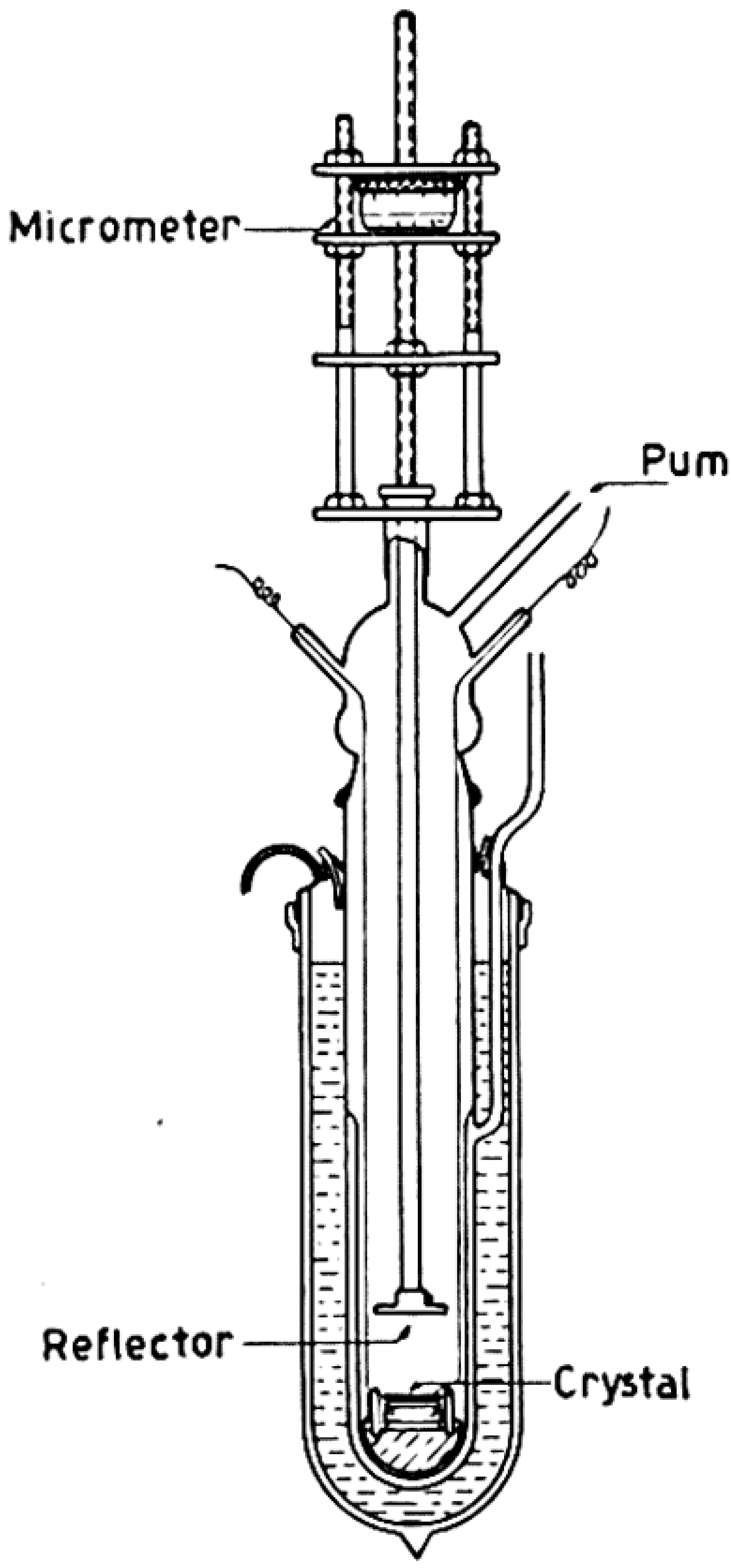

Fig. 57. Interferometer for Low Temperatures (Van Itterbeek *et al.*)

were straight lines at any fixed temperature (down to 60 °K), but in mixtures of two gases, curves were usually obtained.

Van Itterbeek and Mariens [53] have determined also the absorption in oxygen between 373 °K and 173 °K, at various pressures, and Van Itterbeek and Vermeulen V and α in light and in heavy hydrogen between 300° and 60 °K.

In both the latter gases, the absorption is very much greater than the classical value. As pointed out by Bell [54], these Louvain results for absorption, having been all obtained in one and the same interferometer (that of Fig. 57) offer an excellent opportunity for separating the true absorption of the gas α from that due to the resonant radial oscillations α', according to KRASNOOSHKIN [55] (p. 85). For this purpose he plots the measured absorption against p^{-1} and obtains good straight lines (one for each gas and temperature) of which the intercepts represent interferometer absorption.

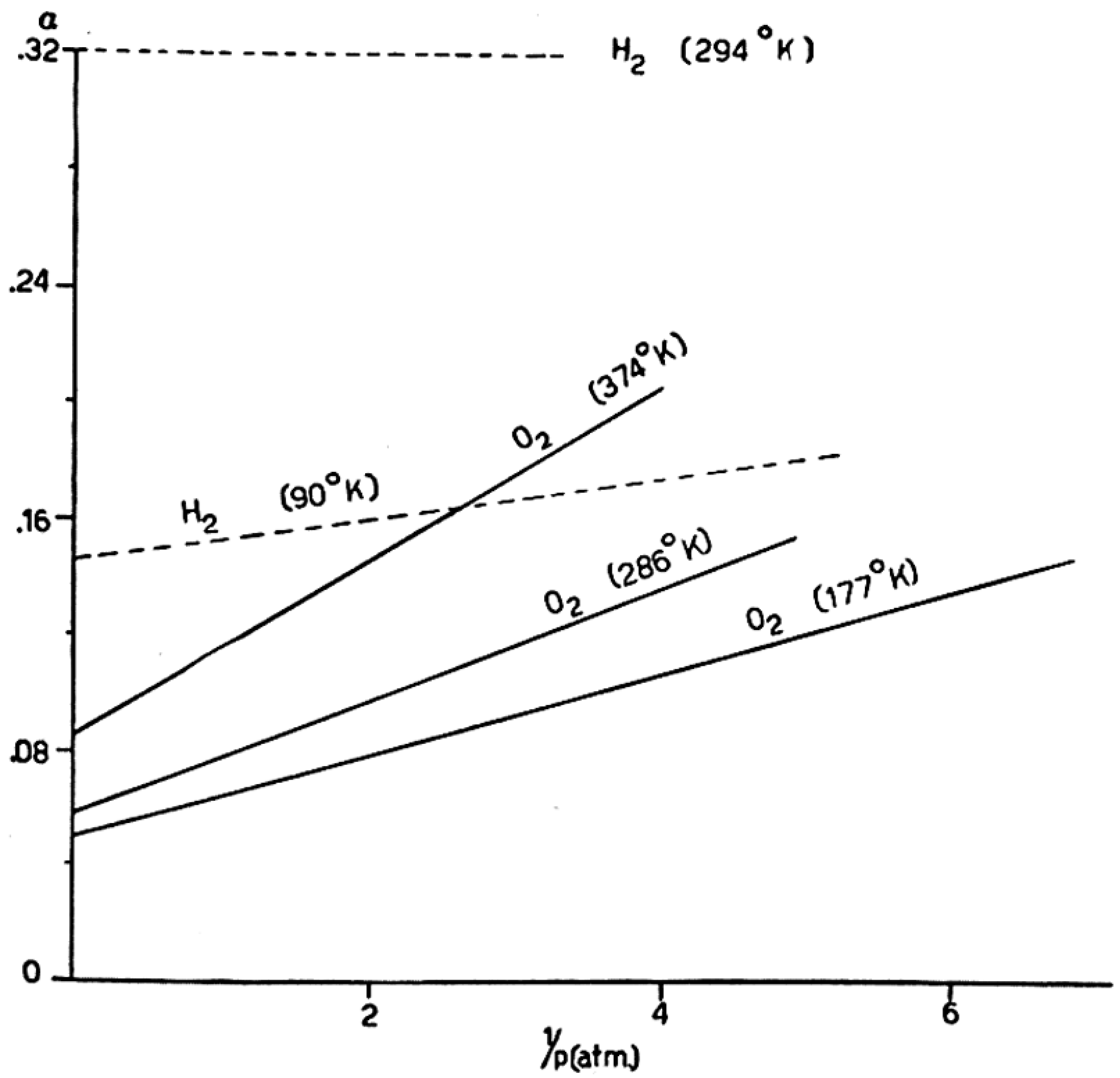

Fig. 58. Absorption Coefficient in Gases at Low Temperatures as Function of Pressure

The results of such plots are shown in Fig. 58. There is a systematic relationship between the gas used and α' (the intercept). For example, for oxygen, α' is greater at the higher temperatures. This is also true for hydrogen, but the values are much greater than those of oxygen. Thus for a given temperature α' varies from gas to gas. The table shows the results of α' and α together with the wave-lengths for the various gases.

Gas	Temp.	λ	α'	α	α (calculated)
Oxygen	374 °K	0.122	0.084	0.026	0.032
Oxygen	286 °K	0.107	0.057	0.017	0.030
Oxygen	177 °K	0.083	0.049	0.013	0.025
Hydrogen	90 °K	0.226	0.145	0.008	—
Hydrogen	294 °K	0.436	0.32	0.000	0.015

The values of α so obtained are almost equal to the classical values within the limits of experimental error, (estimated at 5 % of α'). The values obtained of α for oxygen are considered by BELL to be significantly less than classical values.

To test the theory of KRASNOOSHKIN, α' has been plotted against λ in Fig. 59. The straight line through the origin is at once a confirmation of the theory. It is remarkable that such constancy of operation of the crystal over so wide a range of temperature is obtained. The reason for the lack of correlation between experimental and calculated values of absorption is evident. What was being measured was rather the "interferential absorption" than that of the gas used. As the interferential absorption depends on the particular crystal used, the lack of agreement in results obtained by different observers and between results obtained for different frequencies is so longer surprising. Once the value of $\partial\alpha'/\partial\alpha$ has been measured for the crystal, results at single pressures can be used. The value of this slope deduced by BELL for VAN ITTERBEEK's crystal is 0.7 per cm^{-2}.

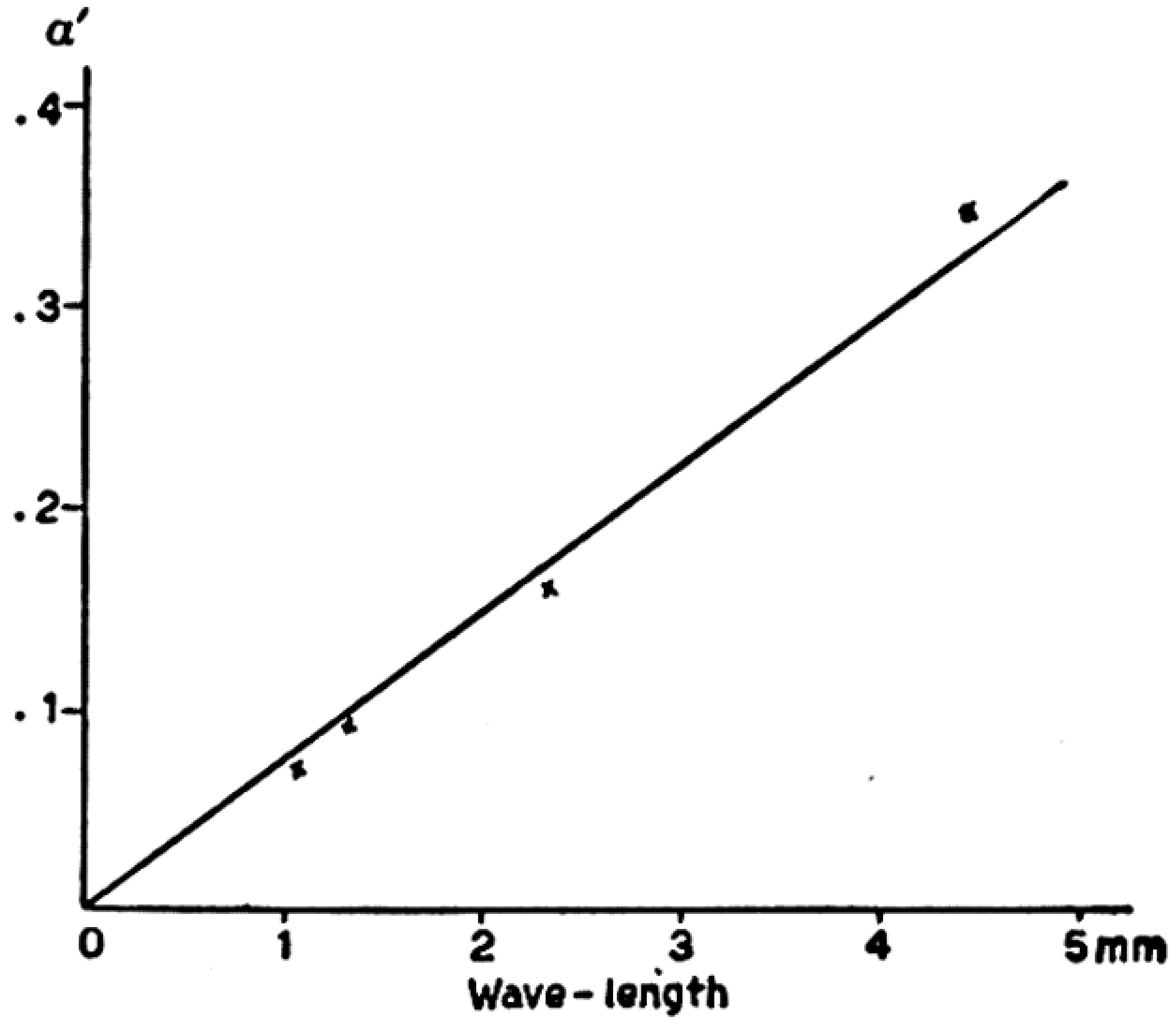

Fig. 59. Absorption as Function of Wave-Length at Low Pressures and Temperatures

9. Propagation in Gases contained in Capillary Tubes

The two aspects which have mainly interested the few workers on the propagation of ultrasonics in capillary tubes have been (1) to test the theory of Kirchhoff in regard to this matter (p. 86), (2) to use the results so obtained to derive propagation constants which, by virtue of the small size of the tube in relation to the wave-length in the gas, shall be independent of the cross-mode modulation discussed in the preceding chapter (p. 81).

A good many experiments have been made on tubes of moderate diameter, down to several millimeters, using audio-frequency sounds. NORTON [56] has pursued the same question into the ultrasonic region. Making use of the fact that thin nickel rods to fit narrow tubes may be set into magneto-strictive oscillation, this author constructed a Pierce interferometer in tubes $\frac{1}{2}''$ to $\frac{3}{8}''$ diameter ($2r$) containing dry air freed from carbon dioxide. The frequency ranges from 10 to 80 kc/sec, and the velocity satisfies the formula:

$$V_r = V_0 \left(1 - \frac{1}{2r} \sqrt{\frac{\nu'}{\pi f}}\right) \qquad (29)$$

when V_0 is the free-space velocity (p. 87). The value of ν' — which KIRCHHOFF deduced by considering the part played in dissipation by true viscosity and by heat conduction — was actually found to be less than the theoretical value (0.47 instead of 0.54) and the author makes a number of suggestions to account for this, of which the most plausible is that some of the heat produced by the passage of the waves is conducted into and through the material of the tube, whereas HELMHOLTZ pictured it as remaining in the gas.

The concensus of opinion is to confirm the KIRCHHOFF theory in this respect. Little has been done, however, at high frequencies in millimetre tubes, owing to the difficulty of getting a source to radiate into such a confined space. MAY[57], however, succeeded in doing this with nickel needles in magneto-striction. The apparatus in principle consists of a magneto-strictive oscillator in a tube provided with a movable piston, the propagation and attenuation constants of the tube being derived from the reactions on the circuit shown in Fig. 14 maintaining the oscillator.

Magneto-strictive rods having diameters from 0.5 to 3 mm were experimented with. The oscillation of those less than 0.9 mm in diameter was so slight and irregular that it was impossible to use them for the purpose in view.

Since thin-walled capillary tubes were unobtainable, and very narrow rods are poor vibrators, composite glass tubes were used; the generator was put in the thin-walled tube having a bore of 1.2 mm and the reflector was moved along inside the thick-walled capillary. In this manner a single generator was made to serve for several capillaries of various diameters. To maintain a stable vibration the rod must be fixed at its centre. The readiest method of mounting is to glue a narrow tissue-paper or cork girdle round the middle of the rod. By sliding the needle into the tube a fairly rigid clamping of this girdle is secured, and at the same time the efficiency of production of the vibrational energy is not impaired by excessive clamping.

The reflectors were made of soft metal (brass and copper) and satisfactory reflecting surfaces were obtained by filing on a fine grindstone. A scheme was devised whereby the reflector would not be rotated as it moved forward under

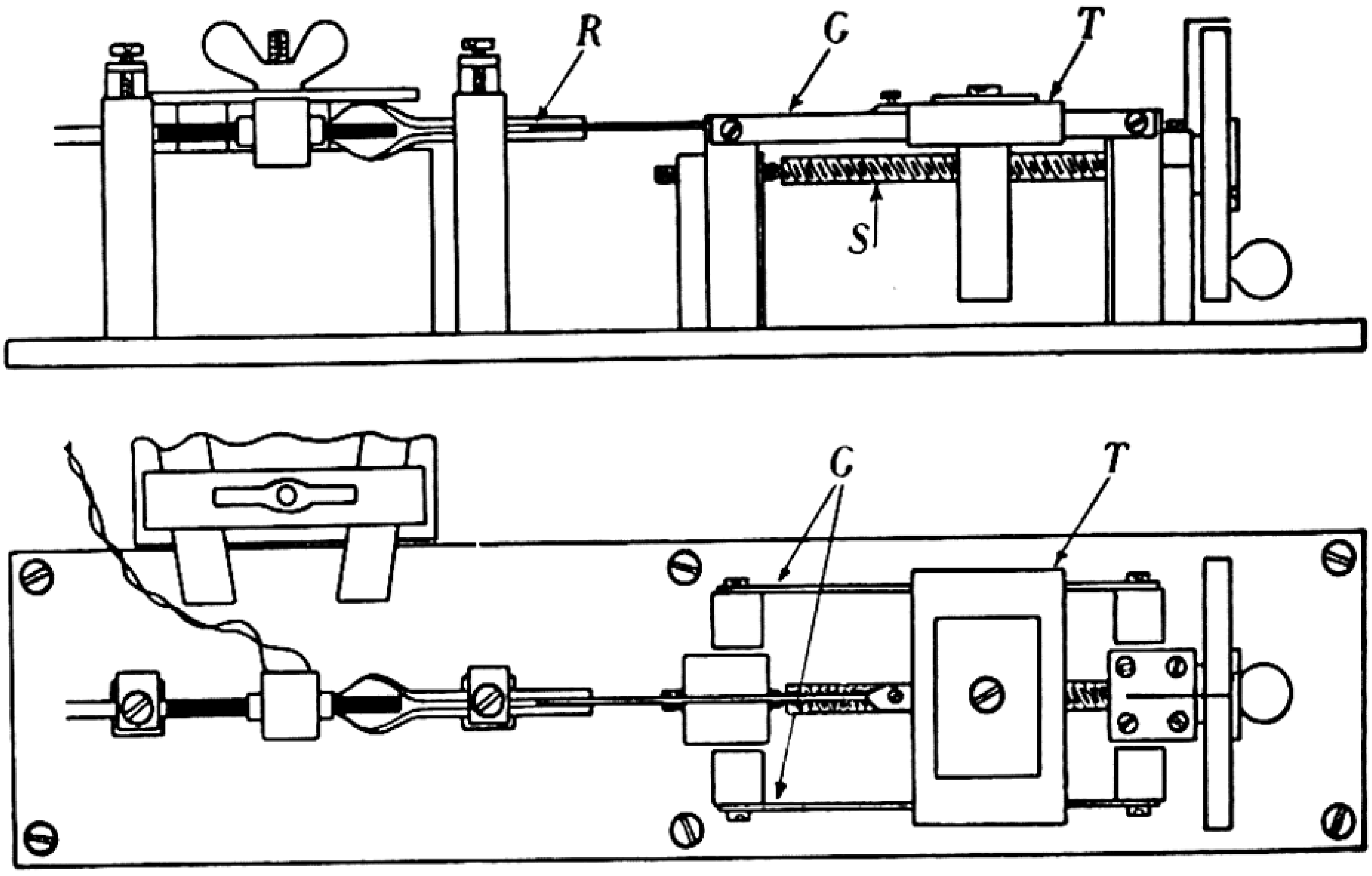

Fig. 60. Interferometer for Gases in Narrow Tubes (May)

the action of the turning handle: the reaction would be withstood by a rigid pillar. A diagram of the interferometer apparatus is shown in Fig. 60. The screw *S* is made to drive a table *T* along a pair of guides *GG*, the reflector R being attached to the table.

As the velocity varies with temperature it is necessary to measure the latter accurately when the velocity of sound is to be measured. Neither a thermometer nor a thermojunction could be introduced into the air enclosure, so the only possible procedure was to place a thermometer or thermocouple near the interferometer, and to satisfy oneself that the temperature measured was actually equal to the temperature of the enclosure. The only methods of supplying heat to the air in the tube and thus altering the temperature would be: (1) joule heating of the exciting coil, (2) eddy-current heating of the source, and (3) direct heating of the air by the radiation. The fact that, within the limits of experimental error, the results of wave-length measurements did not vary as the reflector was moved seemed to indicate that heating of the air in the course of a set of measurements did not appreciably raise the temperature in the tube.

LAWLEY [58] has repeated these measurements using a refined technique. Results in oxygen, nitrogen, hydrogen and carbon dioxide at atmospheric and lower pressures have also been gained. His results for velocity and absorption in air in various tubes ranging in bore from 0.25 to 3 mm

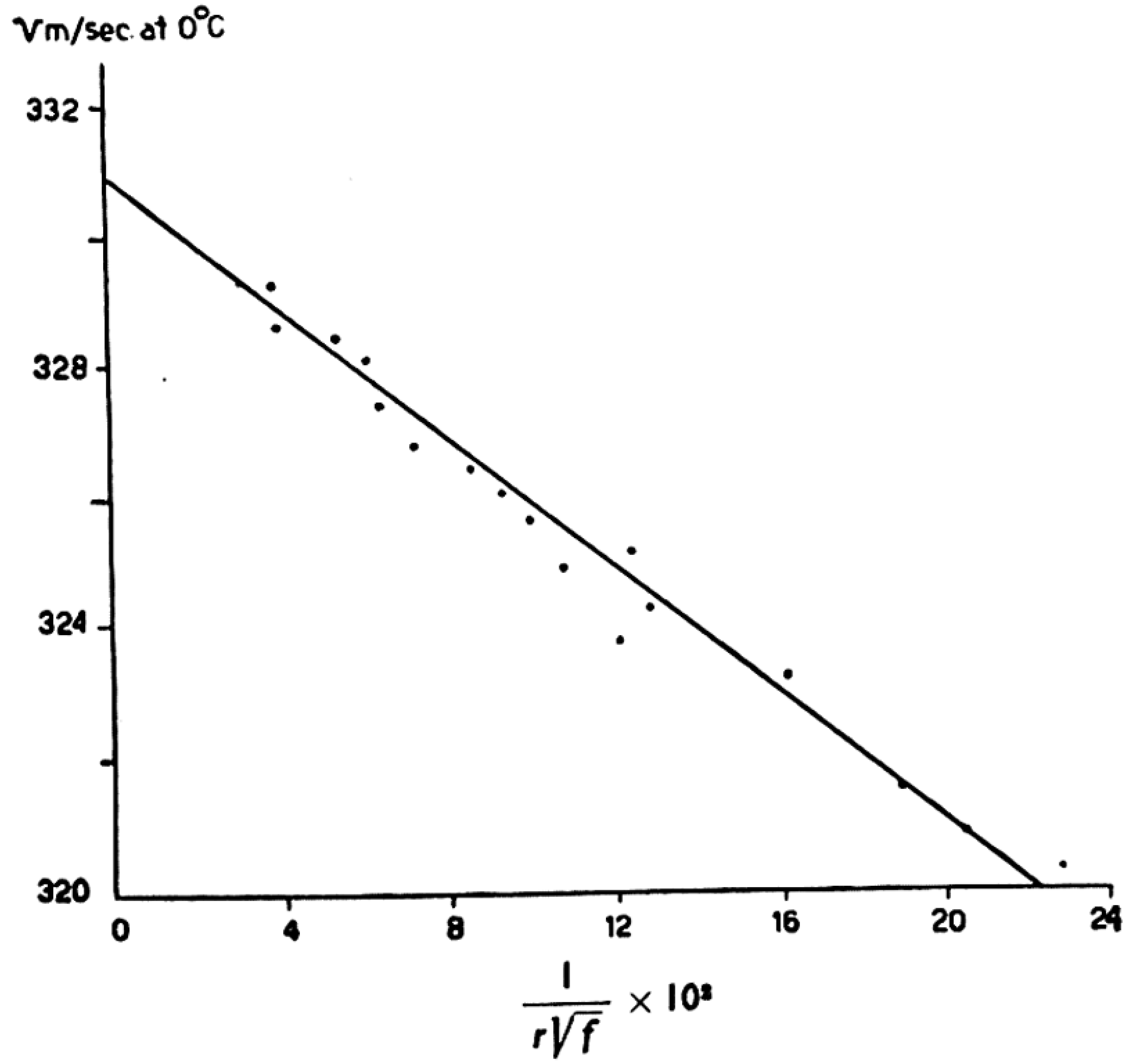

Fig. 61. Velocity in Air as Function of Tube Radius and Frequency (LAWLEY)

Gas or Vapour	At N.T.P.		α per cm at 1 Mc/sec	$\alpha/f^2 \cdot 10^{13}$ Expt.	$\alpha/f^2 \cdot 10^{13}$ Theory	Temp. Range at °C	Press Range atm.	Freq. Range Mc/sec	Note page
	V m/sec	α per cm at 0.1 Mc/sec							
Oxygen	315.5	0.0035	0.3	3	3	−200 to 80	0.1 to 1	0.02 to 1	
Nitrogen	337.6	0.003		3	2.6			0.02 to 1	
Hydrogen	1267		0.06	2	0.2		0.4 to 1	0.5 to 6	114
Hydrogen (heavy)			0.1	4	0.3				
Argon	308				2.7				113
Helium	971				0.075				
Carbon monoxide	337.5		0.5	5	2.3	18 to 2000	1 to 0.1		138
Carbon dioxide	258–270	1	2.7		2.8				113
Nitrous oxide	257–270	0.8	2.65		2.8				113
Nitric oxide	324				2.6				
Sulphur dioxide	209	0.05	0.75	10	3				
Ammonia	415				1.1				131
Chlorine	206				1				
Methane	430				0.11				
Ethane	308				1.4				
Propane		0.005		5	1.65				
Carbon tetrafluoride	171								

Carbon tetrachloride	(132)								
Acetaldehyde	(245)	0.013		13					119
Benzene	(184)	(0.013)		13	1.75				120
Acetone	(192)				6.5				
Hexane (cyclo)	(171)								
Hexane (normal)	(165)								118
Chloroform	(145)								
Ethylene	(320)	(0.028)		28	2				143
Methyl ether	(235)								
Ethyl ether	(173)	(0.025)		25	5.5				
Propyl ether	167								
Methyl alcohol	(305)								
Ethyl alcohol	(230)				37				
*Iso*propyl	(202)								
Methylene chloride	(163)								
Ethylene dichloride	(153)								
Methyl iodide	(143)								
Ethyl iodide	(140)								
Ethyl acetate	(163)				18				

Notes: Values in brackets are deduced from higher temperatures and pressures, experiments at N.T.P. being wanting, *e.g.* because the substance is then liquid.

and at frequencies between 60 and 120 kc/sec are exhibited in Figs. 61, 62. In accordance with theory they are plotted against the parameters $\frac{1}{r\sqrt{f}}$ and $\sqrt{f}/r$ respectively.

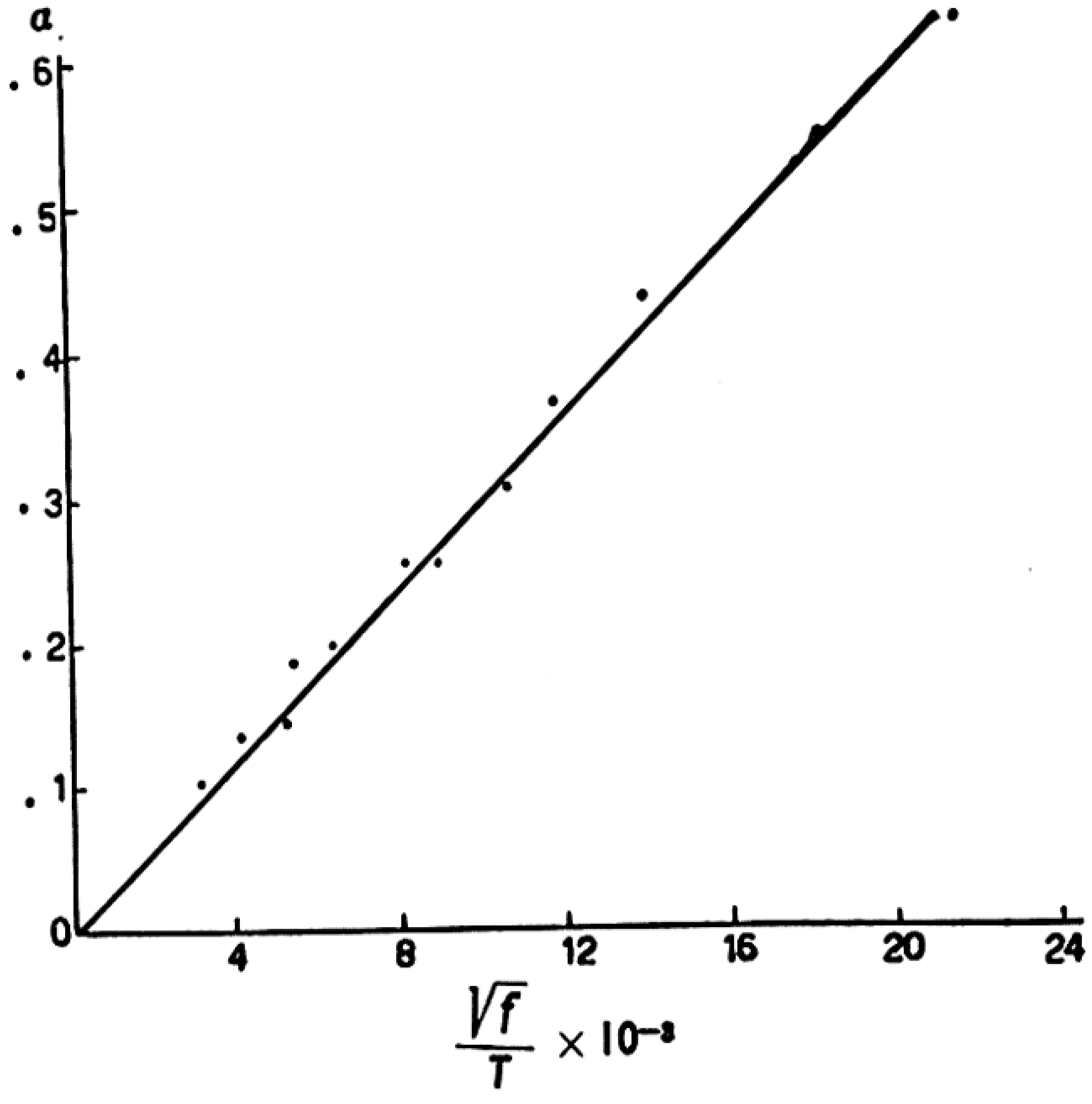

Fig. 62. Absorption Coefficient in Air as Function of Tube Radius and Frequency (LAWLEY)

V decreases linearly with the factor $r^{-1}f^{-\frac{1}{2}}$ of the tube, and extrapolates back to the free space velocity. a plotted against $\sqrt{f}/r$ also gives a straight line which extrapolates through the origin. The coefficients, indicated by the slopes of these lines, fall within a few per cent. of the KIRCHHOFF ones (eqn. 26), using the *static* values of viscosity and thermal conductivity. It appears, therefore, that the high-frequency values of these quantities are the same as the static ones and that no abnormality of "tube absorption" in gases at ultrasonic frequencies is to be suspected.

Since, with the diameters involved, the frequency of the lowest resonant cross-mode (p. 83) lies just above the range of frequency used by LAWLEY, these capillary tubes might be used as interferometers for a study of other gases, without the intervention of radial resonance such as one experiences in wider tubes, due regard being made to the established variation of V and a with r and f.

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CHAPTER V

PROPAGATION IN LIQUIDS

The first extensive measurements in liquids were carried out by using reaction on the source (for velocity) and radiation pressure (for absorption). The Pierce circuit is not so suitable as a circuit employing a Hartley oscillator, because the density of the liquid imposes a load on the crystal which requires more power output[1]. For the same cause, the resonance curve in a liquid is broader; the crystal can even be driven off its natural frequency. Conversely, if it is used as a detector it can so act even if it is not precisely in tune with the oncoming radiation, a fact which has made double quartz interferometers more amenable to use in liquids than in gases.

One of the difficulties which beset all workers with ultrasonics in liquids is the dissipation of the heat generated especially when most of them are bad conductors. Naturally, close watch has to be kept on the temperature of the liquid during the experiments, and in spite of stirring and thermostats, the series of measurements has frequently to be interrupted when the temperature has risen more than one degree. The rate of heating persists while the voltage is applied to the crystal even when the oscillator is put out of tune with the natural frequency. The author suspects that most of this rise of temperature is due to "dielectric heating" and not much to viscous absorption of the ultrasonics. Among the liquids commonly used, it is greatest in nitrotoluene and least in water.

Most measurements of velocity since 1932 have involved the optical diffraction technique, which we have already fully discussed. The advantage is that progressive waves can be used and this obviates the heavy drive on the crystal necessary to get the radiation into the liquid with adequate power to react on the crystal after reflection.

1. Continuous Wave Methods in Liquids

Although the ultrasonic interferometer is as well suited to the measurement of ultrasonic wave-lengths in liquids as in gases, it is dangerous to deduce values of absorption coefficients from the results of such observations unless certain precautions are taken (p. 75). Some means of determining absolute amplitude may be preferred. The means usually adopted have been either (a) radiometers (p. 37), from which the amplitude at any place in the field has been deduced, or (b) light-diffraction measurements, in which the absorption coefficient is deduced from the intensity of the diffracted images of a pencil of light cast athwart the ultrasonic beam, or (c) a hot-wire detector of velocity-amplitude.

Grobe [2] and Biquard [3] attempted to measure the decay of amplitude along an ultrasonic beam in a liquid by comparing the light diffraction patterns at various distances from the source, on the assumption that the intensity of the first diffracted image in the pattern is proportional to the ultrasonic amplitude at the station in question. In view of the difficulty in measuring the optical intensities and complexities in the theory of the effect (*vide infra*), which may invalidate the assumption, it is not surprising that widely differing values for the absorption coefficient in a given liquid are quoted. Nor are the mechanical methods in which amplitude is measured by the pressure on a pendulum in the liquid in much better case, because the presence of a pendulum bob is found to give rise to gratuitous reflections. Probably Buss [4] has brought the technique of the pressure methods to its highest point in his work on the absorption in a stationary wave system, since he has devised a sensitive valve circuit which embodies the pendulum as one side of a condenser. It is amusing to note that while Grobe has no faith in the pendulum method Buss condemns the optical method because he can find no certain correlation between ultrasonic amplitude and diffracted light intensity.

Biquard [3] carried out an extensive series of measurements of absorption in liquids using the pressure vane method and also that just mentioned in which the intensity of the diffracted optical rays is regarded as a measure of the amplitude at the station where the optical crosses the sound path. In using the optical method, he employs a tank of liquid (Fig. 63) irradiated by ultrasonic progressive waves from Q and directs a wide beam of parallel light from S into the whole tank, so that letting each part in turn fall on a photo-electric cell P, he can measure the light intensity.

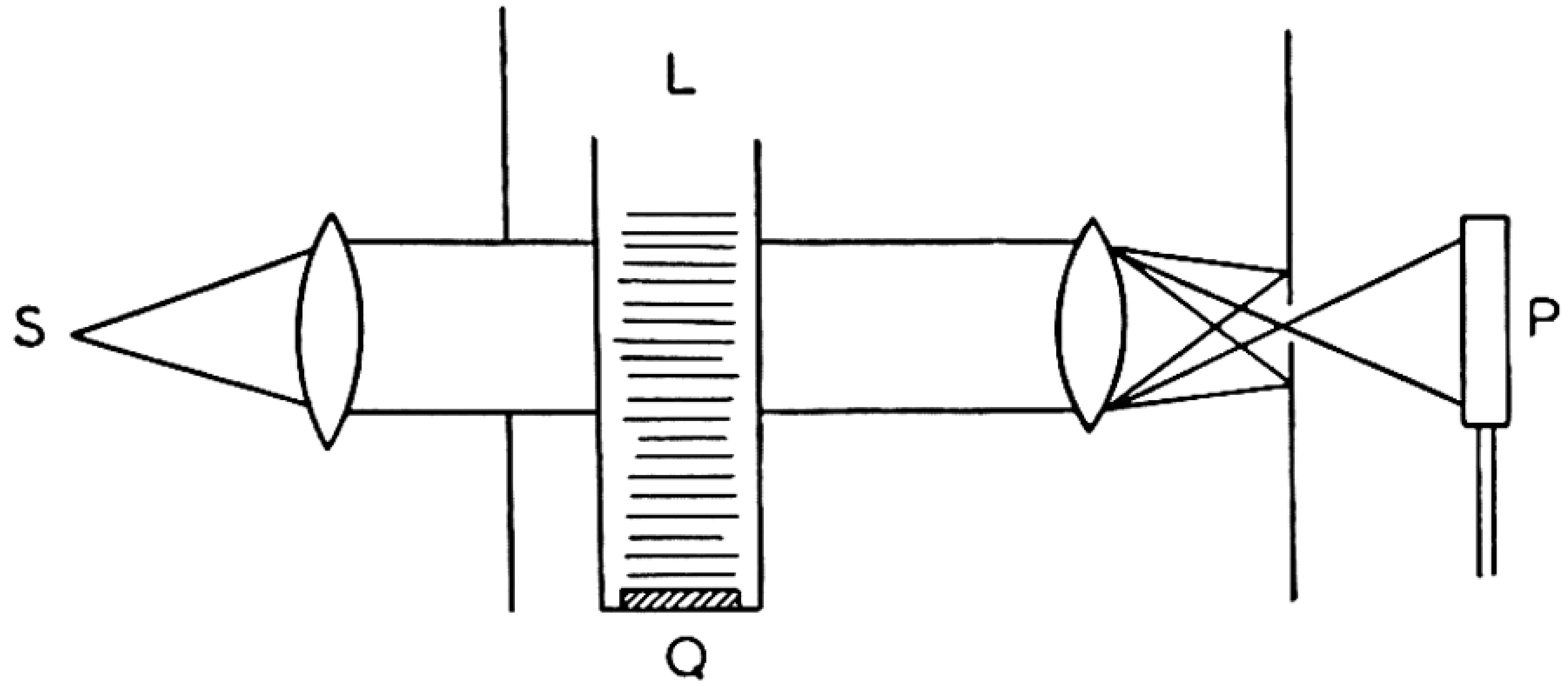

Fig. 63. Apparatus for Optical Diffraction (BIQUARD)

BIQUARD found a relationship between the intensity of light received by the photo-electric cell in the first diffracted "wing" I_x, and the acoustic pressure amplitude, (δp) by varying the power supplied to the quartz.

This relationship proved to be a linear one, but the slope of each line varied with x the distance from the source (in a progressive wave). In fact

$$\log \frac{I_0 - I_x}{I_0} \sim \delta p \cdot x \text{, approximately.}$$

These two expressions calculated from BIQUARD's measurements in benzene are plotted on Fig. 64 and the best straight line drawn among them. From such a calibration, BIQUARD was able to determine α in terms of a plot of $\log (\delta p)$ against x, another straight line.

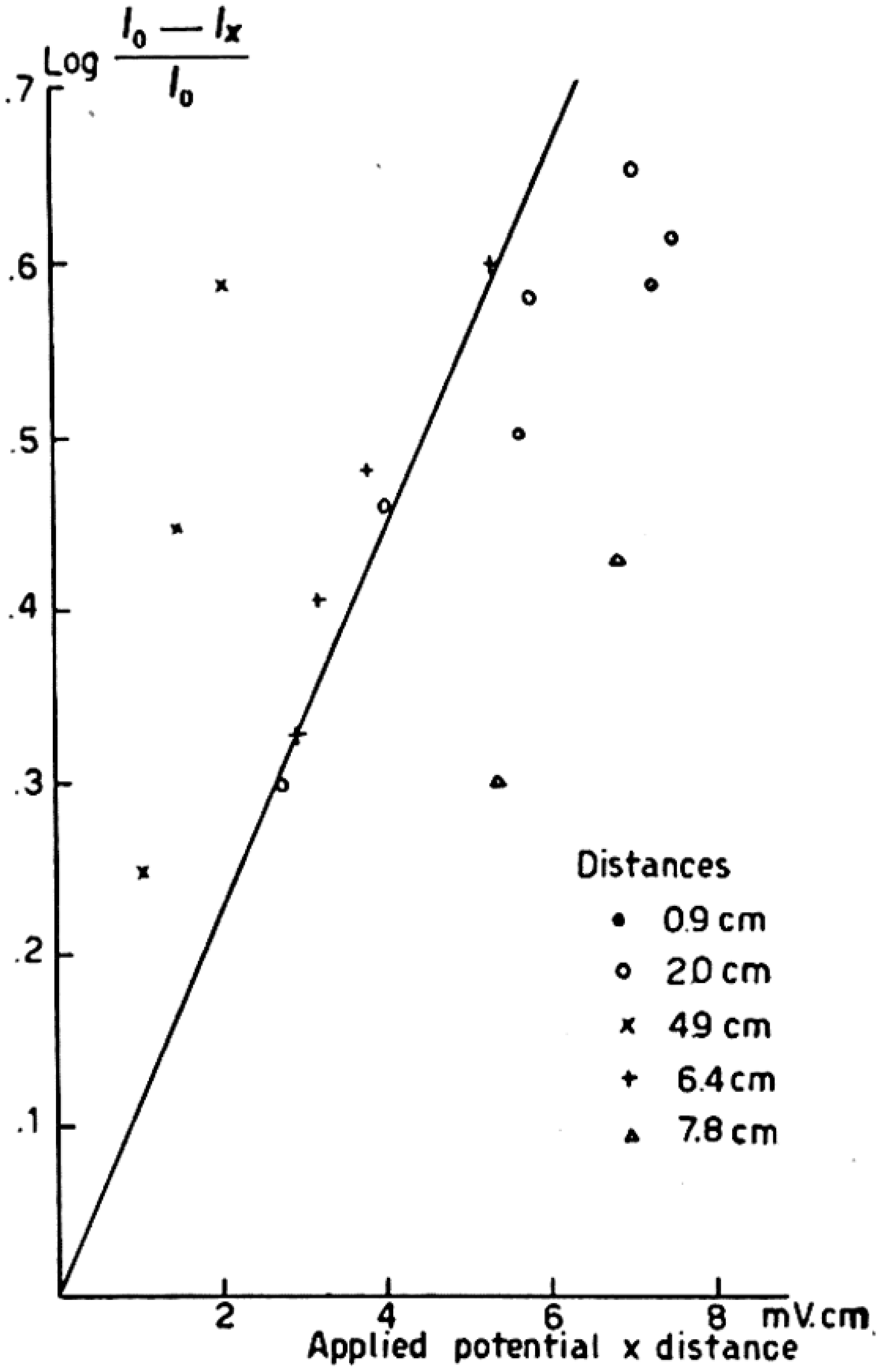

Fig. 64. Diffracted Light Intensity at Different Distances and its Variation with Power applied to Source (After BIQUARD)

It is pointed out that these simple relationships are only true for a small range of acoustic pressure amplitude, as is evident from BIQUARD's results (Fig. 64). Evenso, slight variations in the angle (from 90°) that the beam of light makes with the beam of ultrasonics can produce considerable variations in I_x.

In using either method it is very necessary to ensure constancy of the output during a series of readings of amplitude. BIQUARD did this by letting a derivative of the high-frequency alternating current driving the quartz warm a thermocouple. The rate of rise of temperature was a measure of the power fed to the quartz.

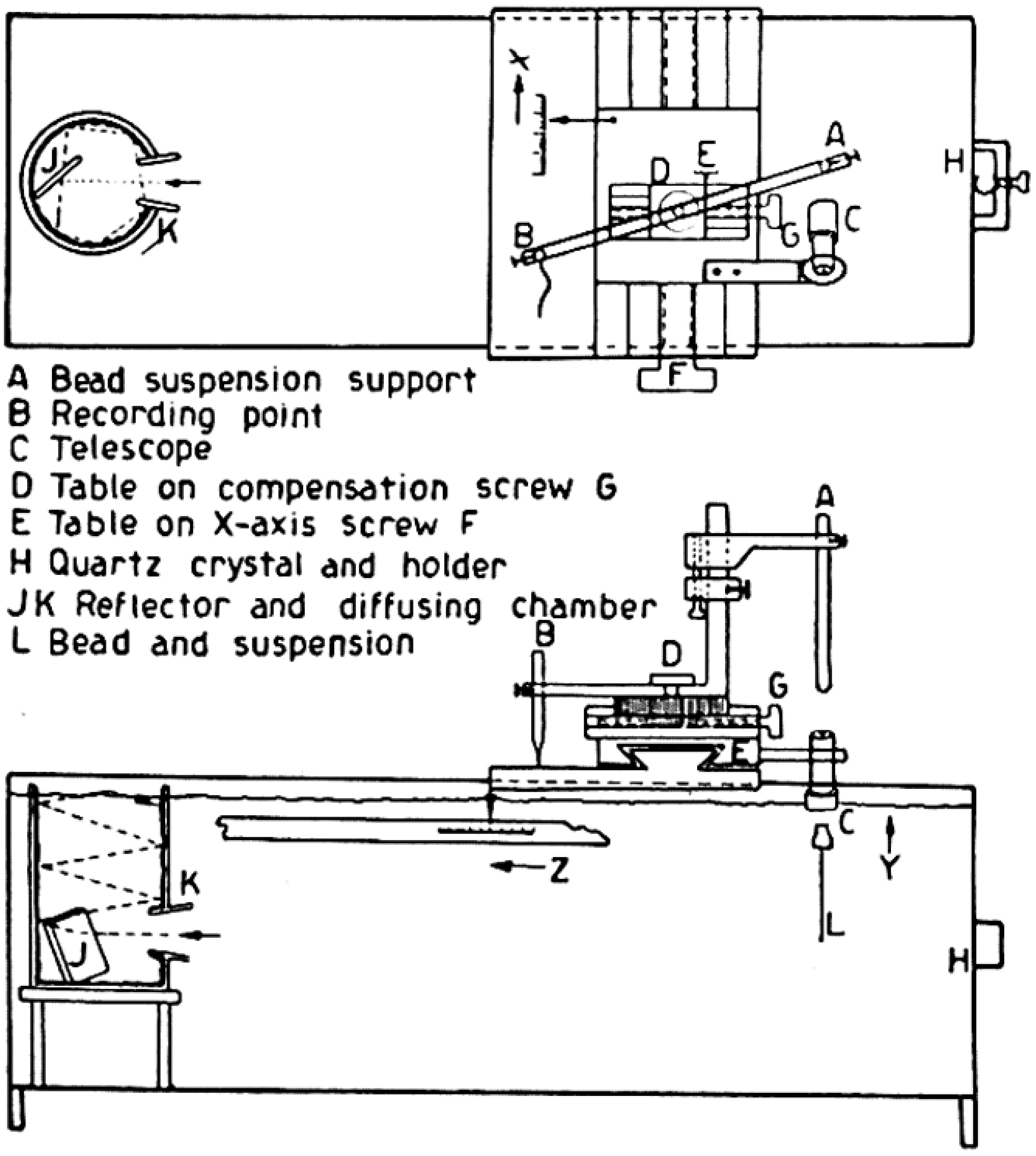
A Bead suspension support
B Recording point
C Telescope
D Table on compensation screw G
E Table on X-axis screw F
H Quartz crystal and holder
JK Reflector and diffusing chamber
L Bead and suspension
A
B
C
D
E
F
G
H
J
K
L
X
Y
Z

Fig. 65. Apparatus Employing Radiometer for Absorption in Water (Fox and Rock)

Fox and Rock [5] have more recently studied the possibilities of a radiometer method for absorption in water. They found it necessary to use quite high power so that the steady fluid current (*cf.* p. 57) which is then set up had to be cut off by a thin collodion film from the region of the radiometer, which consisted of a suspended glass bead. The source was placed in a shield with small aperture, so that direct rays only could fall on the radiometer and not rays reflected from the walls of the tank. The whole apparatus is shown in Fig. 65, which makes clear the device for locating the bead at any point in the field and so exploring the diffraction pattern.

Van Itterbeek and his co-workers, whose results in gases were discussed in the preceding chapter, have turned their attention to absorption in liquids at low temperature, using mainly the pressure-vane method. They prefer to use a small sphere as detector on the ground that reflection from a body of this shape causes least interference with the source as the body is moved along the beam.

A special method, to which we referred earlier (p. 55) has been occasionally employed by them[6]. This consists in driving a quartz immersed in the liquid at a range of frequencies each side of resonance and measuring the relative power required for the same amplitude. Flat-topped resonance curves are so obtained, from which the damping of the system quartz plus liquid is calculated. The theoretical decrement is $2\varrho c/\varrho_0 c_0$, (p. 54) but was found to depend also on the mounting of the quartz. The method is however only susceptible to use when the liquid is very viscous and so presents great damping.

Rieckman[7] measured ultrasonic absorption in mercury using the torsion vane method. Even so, it was necessary to suspend the vane in another liquid (water) and to let the energy which had traversed a given stretch of mercury pass through a "window" into the water to fall upon the torsion arm. The material of the window must have a specific impedance intermediate between that of mercury and that of water. Actually mica was the substance chosen as fulfilling this requirement. Nevertheless, the window had a reflection coefficient of about one half and the energy sent back had to be absorbed. This was done by putting a coating of pertinax paper over the surface of the iron trough containing the mercury. Around the walls of the chamber holding the torsion balance a rubber sheet served a similar purpose. The divergence of the beam from the forthright direction out from the quartz is investigated by this author. Of course, the absorbent lining is helpful too in this respect but it is well to remember that, on account of the greater ratio of wave-length to aperture of source, such divergence with consequent missing of part of the beam by the detector — in this case, the vane — is a more frequent cause of error in absorption measurements in liquids than in gases. The frequencies used by RIECKMAN consisted of the series of harmonics lying between 20 and 55 Mc/sec of the fundamental 7.5 Mc/sec.

The author has found the hot-wire method suitable [8]. The apparatus is sketched in Fig. 66. The quartz oscillator in the form of a disc rests on a brass plate forming the base of a glass vessel to which it is cemented, and radiates vertically. The base forms one of the electrodes. The upper one is a piece of tinfoil with which an insulated lead down one side of the vessel makes contact. The reflector, of fibre, is carried by a threaded rod, tapped to fit the cover of the vessel, carrying a graduated head on its upper end. The hot-wire is mounted on the ends of two fine needles

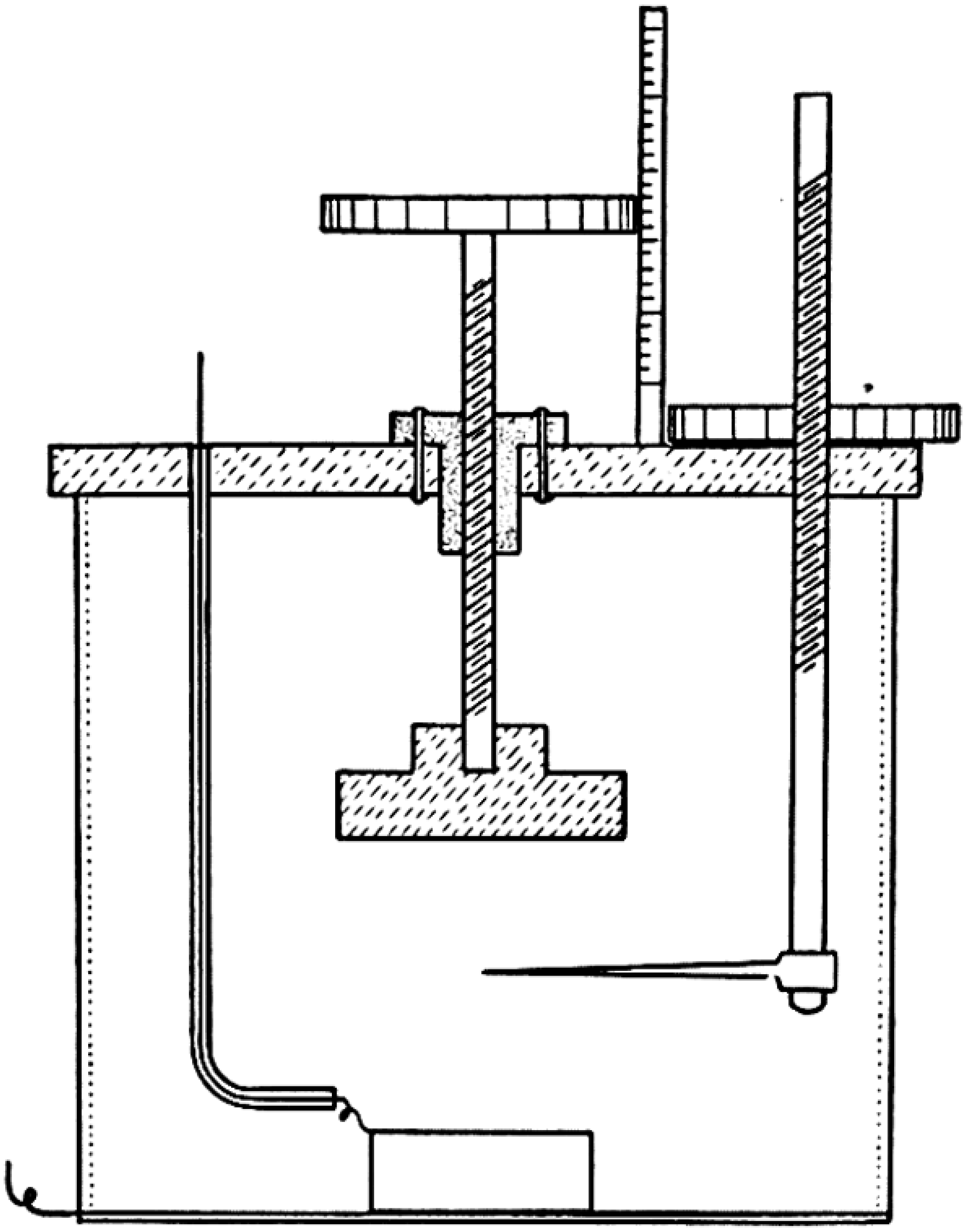

Fig. 66. Hot-Wire Interferometer for Liquids (RICHARDSON)

which pass through a fibre strip and is also capable of fine adjustment by means of a knurled head and graduated disc on the cover. To supply the crystal a Hartley generator was used, employing a pair of T 55 valves and an anode potential of 1500 volts at 0.1 amp. The tunable part of the circuit consisted of two Sullivan oil-filled condensers in parallel, of maximum capacity 0.001 and 0.0001 mfd respectively, and a coil allowing of tappings to give fixed inductances between 0.003 and 0.3 mh. A wave meter, guaranteed to 0.1 per cent, told when the oscillator was in resonance with the crystal. The actual supply of power to the crystal was kept as low as possible, consistent with obtaining a measurable response of the hot-wire detector, and was never sufficient to give any signs of a disturbance on the surface of the liquid, when the reflector and its support were removed from the vessel.

To prevent any radiation which had struck the walls returning to the body of the liquid, an "absorbent" lining consisting of a layer of fine gauze was draped round the interior of the vessel close to the glass walls and under the lid.

Since the quartz would not oscillate under water it was placed under another liquid dielectric with a layer of distilled water above. After trying for this purpose a number of liquids having a specific acoustic impedance nearly matched to that of water, nitrotoluene was found most efficacious for this purpose.

To measure the wave-length of the ultrasonic radiation in a liquid the hot wire was set at a fixed distance (usually about 15 mm) from the upper face of the crystal, and the reflector was moved to or from the hot-wire. Maxima in the readings of the current from the hot-wire amplifying valve also occurred at regular spacings of a half wave-length. The reflector was then fixed at an integral number of half wave-lengths from the radiating face of the crystal, and the hot-wire moved along a vertical traverse between them, readings being taken every fifth of a millimetre.

In this and in a number of other measurements in the lower ultrasonic range, the sound field in front of the quartz was explored and due correction made for diffraction and for the finite size of the reflector in relation to the spreading of the beam (Fig. 24, p. 52). This can account for a considerable fraction of the "apparent" attenuation.

2. Pulse Methods for Absorption

In the last five years quite a number of investigators have used the pulse method. BIQUARD and AHIER [9] did little more than establish the technique but extensive results particularly of absorption have come from PELLAM and GALT [10] and from PINKERTON [11].

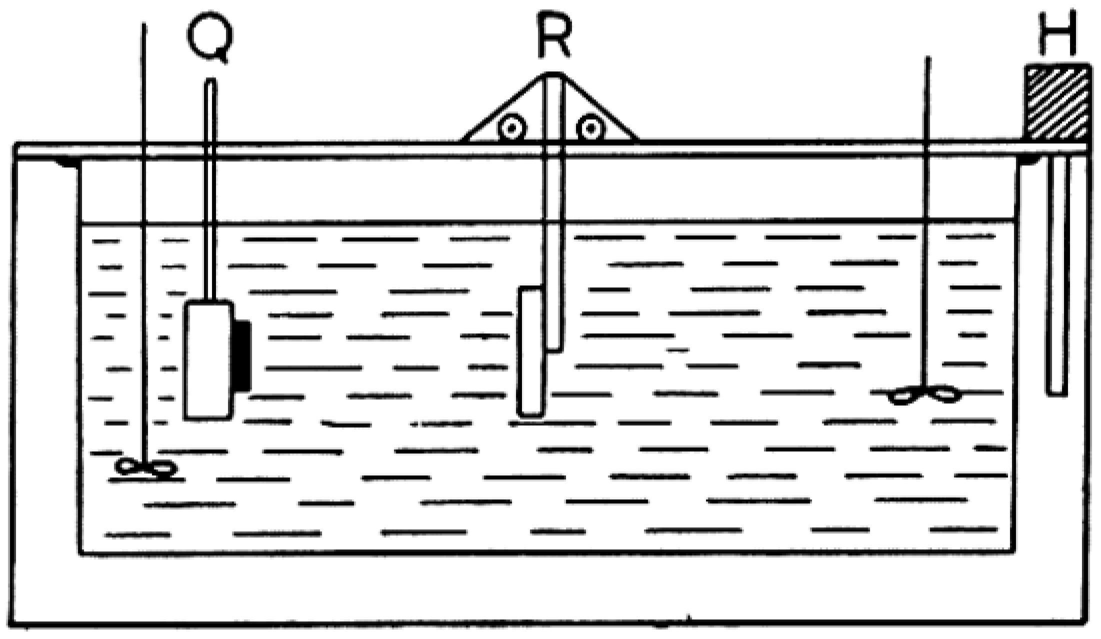

Fig. 67. Pulse Method for Absorption in Liquids (PELLAM and GALT)

The former's apparatus is sketched in Fig. 67 for a liquid in a cell contained in a water cooling tank. The quartz *Q* is hung by its lead at one end of the cell, while the reflector R can move on rails over the top of the tank. The liquid inside is stirred and the heater and thermostat *H* maintains the temperature of the cooling water.

In order to avoid obscuration of the image of the reflected pulse on the screen by multiple echoes, PINKERTON restricts the aperture of the sending crystal by an iris in the form of a truncated cone with a hole bored through the narrower end so that sound striking the slant edge is turned aside, while sufficient energy enters and leaves the hole to give the optimum echo signal and ensure that the reflector lies in the Fraunhofer region. The latter condition limits the ratio of the size of the aperture to that of the crystal face (*cf.* p. 48). The ratio of emitted to returning intensity can then be made as large as necessary. Since PINKERTON, alone of those using the pulse method, corrected his results for diffraction, following the treatment of BORN (p. 53), his results for absorption are probably the most accurate with this method.

The power required to be put into the liquid is quite small; although the peak power may be large, the mean power in the pulse can be only $\frac{1}{500}$th of the maximum. Because it is only turned on for the duration of the pulse, $\frac{1}{500}$th of the pulse repetition period, heating effects are minimised, which makes it quite possible to operate a quartz in one of its upper harmonics. RAPUANO [12] for instance, has reached the enormous frequency of 280 megacycles/sec. At such frequencies, however, the absorption is so great that to get the pulse returned with adequate amplitude, the reflector must be very near the source which introduces difficulties in switching the quartz circuit from a "sending" to a "receiving" condition. RAPUANO overcomes this by using for the reflector a cylinder of quartz instead of the usual disc (Fig. 68). This forms an acoustic delay line, for if the liquid and quartz are well-matched the radiation will enter

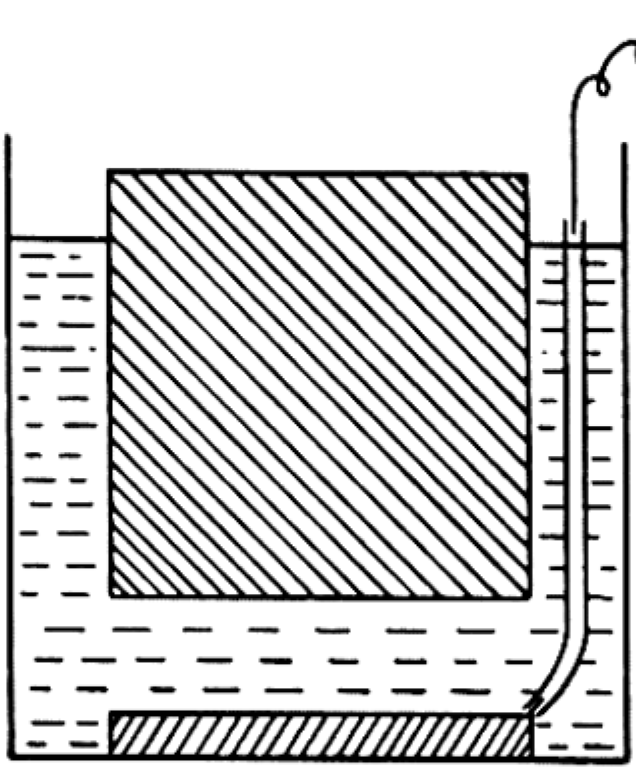

Fig. 68. Acoustic Delay Line in Liquid Medium (RAPUANO)

at the base of the cylinder, be reflected at its summit — which is exposed to the air — re-enter the liquid at the base and so return to the source. With this device liquid paths as short as 10 microns have been used. Allowance must, of course, be made for attenuation in the solid.

3. Reverberation Methods for Absorption

MULDERS [13] describes a reverberation method for the absorption in liquids. Sound waves of frequency ½ to 1½ Mc/sec are generated from a crystal of natural frequency 1 Mc/sec hanging in oil in a thin-walled glass tube through which it radiates into the experimental liquid. A receiver (crystal microphone) is mounted on the floor of a tank containing water. After the source has been stopped, the sound reverberates in the vessel and is meanwhile picked up on the microphone, as in the familiar technique of room acoustics.

To smooth the decay curve free from interference effects, owing to the setting up of standing waves in the liquid, the source is "warbled" through a range of 15 kc/sec at a rate 200 times per second, copying another technique of room acoustics.

The signal is exhibited on a cathode ray oscillograph against an exponential time base. From the mean decay curve — approximately a straight line — of the signal, the attenuation is calculated, as the time for the amplitude to fall through a known fraction. Allowance has then to be made for reflections from the sides and free surface in estimating that due to the liquid [14,15].

Meyer has shown that in cylindrical vessels the reverberation time (T) varies;

(1) when the height (h) of the liquid is varied, in accordance with the empirical formula:

$$\frac{h}{T} = C_1 + C_2 h\,.$$

(2) when the radius a of the vessel is varied, in accordance with the formula:

$$C_2 = a + \frac{C_3}{a}\,.$$

(C_1, C_2 and C_3 are constants for a given liquid).

By varying a it is thus possible to calculate α.

The thickness of the walls might be expected to affect the reverberation time but in fact did not. Apparently they acted as completely rigid walls in Mulders' experiments. Nevertheless, these apparatus absorption factors are considerable compared with that due to the liquid, which is actually sought.

4. Absence of Dispersion of Velocity in Liquids

ZACHOVAL [16] claims a dispersion of one per cent. between the first and third harmonics of a source of 2 Mc/sec working in resin oil, while toluene, nitro-benzene, and glycerine show a fall of velocity between 1 and 3 Mc/sec though only of the order of one or two per cent. The Indian investigators [17] use higher frequencies (from 1 to 13 Mc/sec) in benzene, carbon tetrachloride and disulphide, and glycerine. Their results show no certain dispersion in this region in either carbon tetrachloride or distilled water. In the latter KRISHNAN [18] attained a frequency of 22.5 Mc/sec without noticing a change in velocity. But a number of other writers consider that the small amount of dispersion which they have noted in liquids is rather to be ascribed to technical difficulties in carrying out the experiment. Both MATOSSI [19] and SCHREUER [20] remark that the velocity — and so too the dispersion as between values at different frequencies — is a function of intensity. The latter can be raised through the coupling between the quartz source and the valve oscillator which maintains it. When this was done (in water or xylol) with two sources of 3 and 10 Mc/sec respectively, "dispersions" of velocity with frequency could be produced greater than any observable between the results for the pair of sources under equal coupling. Using the optical technique, SCHREUER also found that the velocity depends on intensity of source. Other troubles which affect the apparent velocities were traced to distortions in the sound field caused by irregular temperature effects and resulting departure of the wave-fronts from plane form. On extrapolating his results to zero intensity, he could establish no dispersion greater than 0.01 per cent. Curiously enough, the velocity in water rises by 0.04 per cent. as the intensity of the source is increased by a factor of five, but in several organic liquids it goes down as the power supplied to the source is raised. The measured dispersions fall often within the limitations of wave-length measurements, always difficult at such high frequencies.

Here we may draw attention to another rather indirect way in which a velocity of sound in a liquid may be derived, indirect in the sense that it is deduced purely from optical data. It is based on an assumption of BRILLOUIN[21] (*vide* Chap. VII) that the spontaneous thermal agitations in liquids involve acoustic waves — owing to local changes of density — of mean length λ which when irradiated with monochromatic light of wave-length l causes diffraction in accordance with the well-known ("Bragg") formula:

$$l = 2\,\mu\lambda \sin\theta/2\,, \tag{30}$$

θ being the aspect angle and μ the refractive index of the liquid to the light. It is therefore similar in principle to the method of LUCAS and BIQUARD, p. 76, except that no *ad hoc* sound waves are concerned and λ is an inconstant fluctuation about a mean. Such "Doppler shifts" have been observed when a liquid (untouched by sound) is irradiated by light in an optical interferometer (Fabry-Perot etalon). B. V. R. RAO[22] demonstrated this in carbon tetrachloride.

By making an estimate of λ from these shifts and multiplying by the frequency of the light used he arrives at values for what he calls the "hypersonic velocity" in this liquid of 1070 m/sec, against the ultrasonic value of 928 m/sec. It is admitted however, that this technique is very imprecise at present [23]. In fact other workers such as Venkataswaran [24], Rank, Shull and Ansford [25] have concluded, in repeating the experiment in acetone and in carbon tetrachloride, that the hypersonic agrees with the ultrasonic velocity.

At higher temperatures the method fails to yield definite Brillouin lines, the assumed ordered structure of thermal waves breaking down into disordered fluctuations of incoherent frequencies. This is especially noteworthy in glycerine which behaves almost as a solid to hypersonic frequencies when its viscosity is large, but at higher temperatures exhibits a velocity of propagation like that of a liquid.

A number of attempts have been made to correlate the propagation constants (to sound) in a liquid with other known molecular properties.

Thus M. R. Rao [26] has pointed out that in many liquids, the cube root of the velocity of sound is inversely as the molecular volume v. Rao finds in fact that if one divides the temperature coefficient of velocity of sound $\partial c/\partial\theta$ into the coefficient of volume expansion one obtains a constant (—3). Thus $\frac{1}{v}\frac{\partial v}{\partial\theta}\Big/\frac{1}{c}\cdot\frac{\partial c}{\partial\theta} = -3$; whence vc^3 is constant at all temperatures.

When the temperature changes, the density and temperature are related to their values at the critical point — indicated by suffixes — by an equation of the form $\varrho = \varrho_0 (1 - \theta/\theta_0)$. Whence it follows that the velocity of sound in a liquid follows a law: $c/c_0 \equiv (1 - \theta/\theta c)^{3/10}$.

One can examine the same question from the aspect of the symmetry of different molecules or — in the case of organic liquids — of their position in a series. Every addition of a CH_2 group in a homologous series increases RAO's constant by the same amount, making it proportional to the molecular weight.

PARTHASARATHY [28] has experimented on many liquids, but SCHAAFS [29] who has analysed the results maintains that they do not show — as PARTHASARATHY maintains — that aromatic substances have a generally higher velocity than aliphatic. Increasing density through a homologous series ought to decrease c, but, in fact, does not. In halogen compounds the abnormal increase in molecular weight accounts for the observed fall in c through a series. Increase in molecular volume and the density go hand in hand. These are the factors which cause the increase of c when heavier atoms are substituted in esters, and not increase in molecular weight *per se*. There is no real evidence that dipole moment is of importance in this connection.

5. Attenuation in Liquids

While dispersion is dubious, there is no doubt about the large attenuations which have been observed. While there are discrepancies in the values for α obtained by different workers on the same liquid, all are agreed that α/f^2 far exceeds the "classical" value, especially in liquids like carbon disulphide, carbon tetrachloride, and benzene.

In most liquids α/f^2 is however constant at a given temperature. Only in acetic acid has a decreasing α/f^2 with frequency been confirmed (Lamb and Pinkerton[30]). Fig. 69 compares methyl alcohol and acetic acid in this respect and Fig. 70 shows results for water (after Teeter[31]).

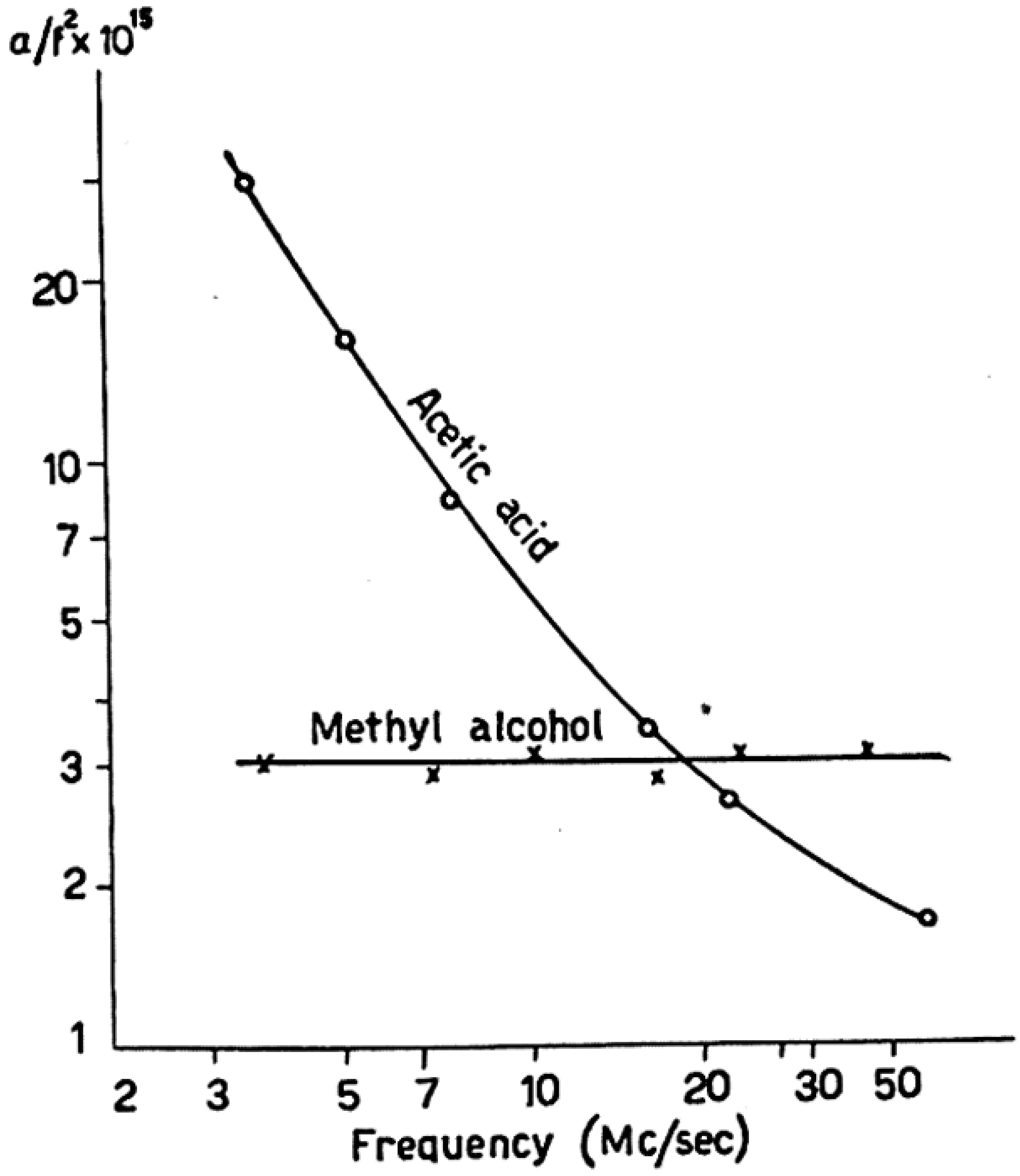

Fig. 69. Absorption as Function of Frequency in Methyl Alcohol and Acetic Acid

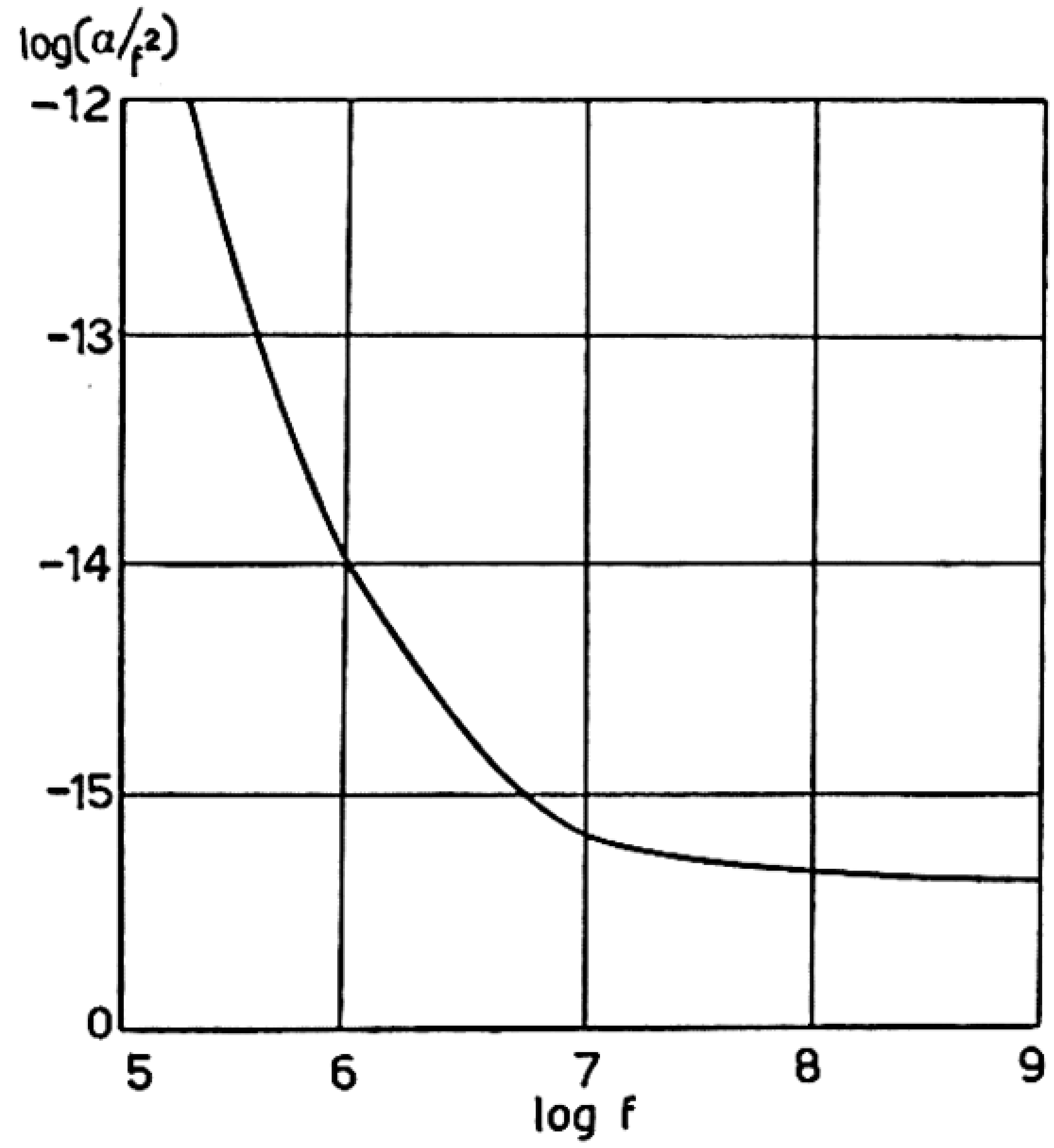

Fig. 70. Absorption in Water as Function of Frequency (TEETER)

HUZZARD [32] has obtained absorption results (by optical diffraction) in pairs of organic liquids having symmetry of molecule (such as benzene, toluene) without finding any correlation. All that can be said is that the addition of a CH_3 group causes an enormous increase in absorption whereas subsequent additions or re-arrangements have little effect. Dissolving either of the afore-mentioned substances in polystyrene produced no change in α although it increased the viscosity enormously; obviously the absorption in this case is a molecular effect.

Where discrepancies in values of α exist it is usually found that those methods which require the more intense sources for their operation give the higher values for the coefficient. Neglect of diffraction losses also gives high attenuation.

6. Results for *V* and *α* in Liquid Mixtures

If two liquids of different density and elasticity are mixed in various proportions, one would expect the velocity to pass gradually from the value corresponding to one pure liquid to that of the other.

To deduce the velocity of sound in a mixture of two fluid media, we shall assume that the velocity is the same as that in a homogeneous fluid of the mean density ϱ and mean elasticity E as in the mixture. Let ϱ_1, ϱ_2 and E_1, E_2 represent the density and elasticity of the respective constituents. Then let x be the proportion of the first constituent by volume and $(1 - x)$ the proportion of the second constituent by volume. The mean density ϱ is therefore $x\varrho_1 + (1 - x)\varrho_2$. The mean elasticity E is related to the component values by

$$\frac{1}{E} = \frac{x}{E_1} + \frac{(1-x)}{E_2}\,.$$

Whence the velocity * of the mixture:

$$c = \sqrt{\frac{E}{\varrho}} = \sqrt{\frac{E_1 E_2}{\{xE_2 + (1-x)E_1\}\{x\varrho_1 + (1-x)\varrho_2\}}} \qquad (31)^*$$

The attenuation: concentration curve also should continually increase or decrease from one extreme to the other, insofar as the viscosity of the mixture behaves in the same way.

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* *cf.* A. B. Wood, *Sound*, p. 361.

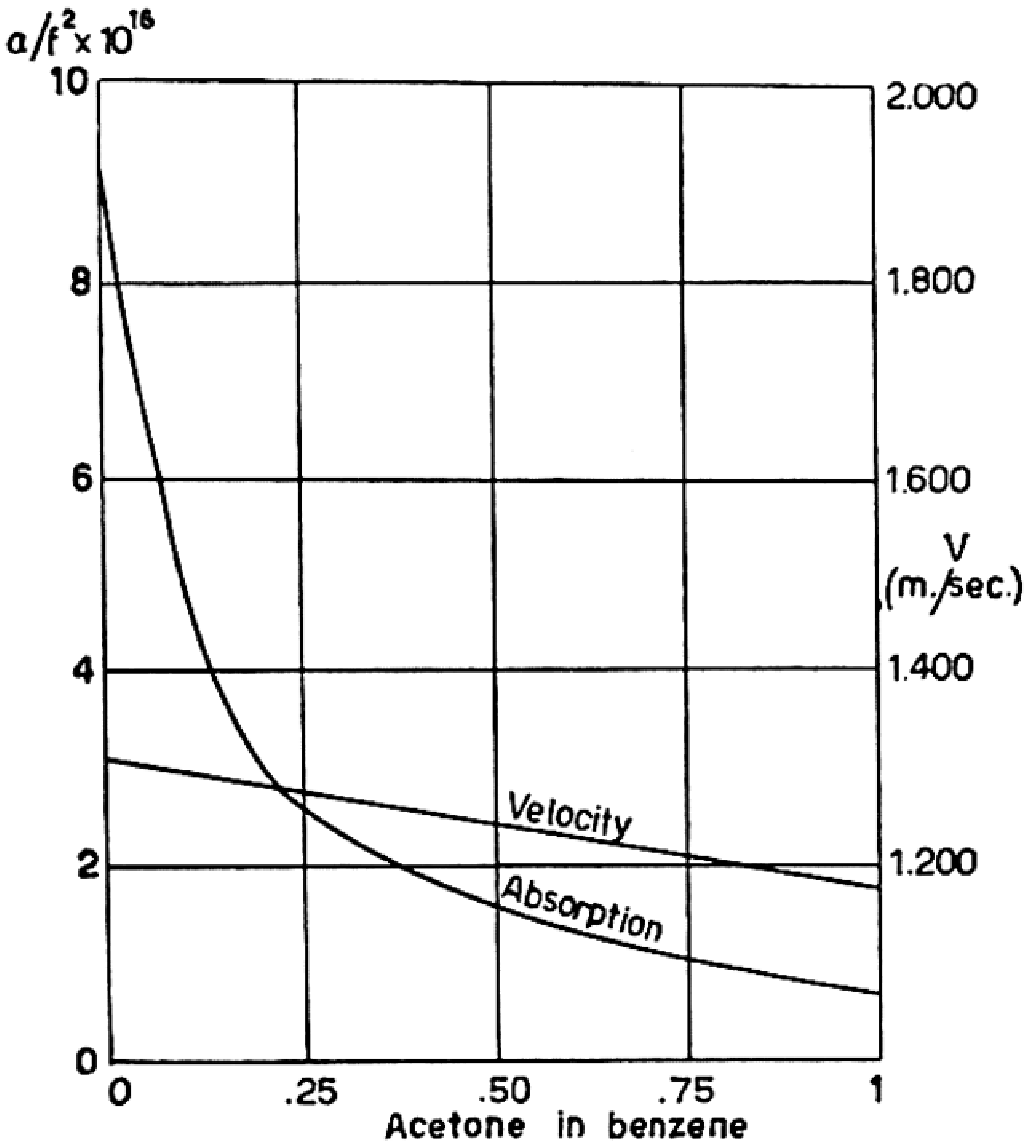

Fig. 71. Velocity and Absorption in Acetone-Benzene Mixtures (WILLARD)

In fact, some mixtures do this, *e.g.* Fig. 71 shows WILLARD's [33] results in acetone-benzene mixtures. In other mixtures, however, the viscosity reaches a maximum at some intermediate concentration, and this affects absorption and velocity too. BURTON's [34] results in acetone-water mixtures are shown in Fig. 72 together with (broken line) the "classical" trend of the absorption. The slight hump on the theoretical absorption curve is due to the fact that the viscosity has a maximum for a nearly 50 : 50 mixture, but it is obvious that this cannot explain the huge hump on the observed attenuation : concentration curve.

Aqueous electrolyte solutions on the other hand show

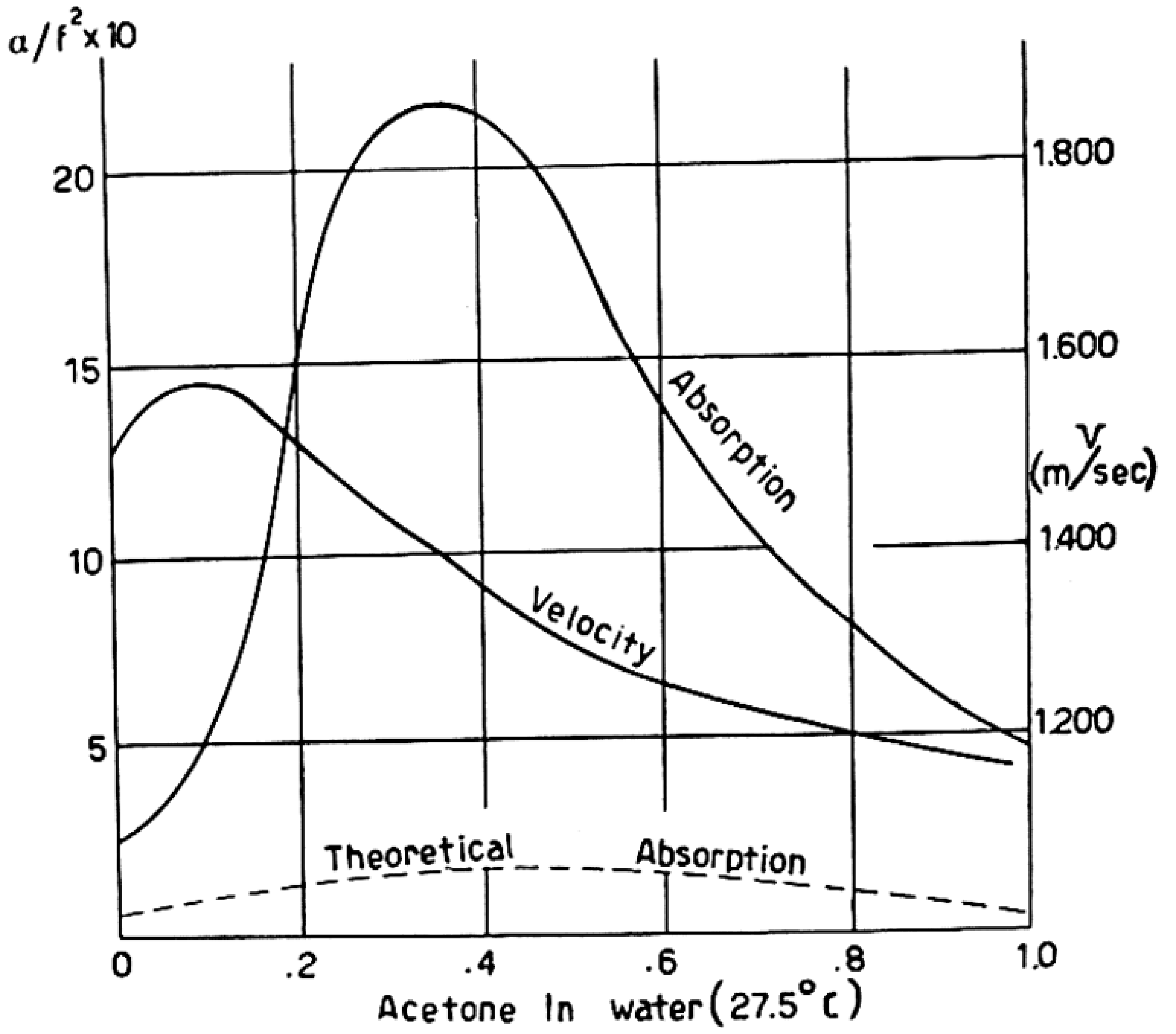

Fig. 72. Velocity and Absorption in Acetone-Water Mixtures (BURTON)

an almost linear change of α^2 with concentration though there is a tendency for α/f^2 to decrease at higher frequencies. The slope of this factor (with concentration) depends on the two ions involved. The table below (due to RÜFER[35]) gives the absorption of molar solutions relative to the solvent water, which is made equal to unity for the purpose

H_2O	1	CH_3COONa	1.12	$NaCl$	0.89
Na_2SO_4	2.54	$Cu(NO_3)_2$	1.11	Na_3PO_4	6.15
$CuSO_4$	5.28	$MgCl_2$	1.09	$K_4Fe(CN)_6$	2.95
$MgSO_4$	4.40	$CuCl_2$	1.93	K_2CrO_7	2.20
$NaClO_4$	1.37	KBr	0.88	$K_2Sn(OH)_6$	2.30
$NaClO_3$	1.05	$NaBr$	0.85	$NO_2(NO_3)_2$	3.02

of comparison. GIACOMINI and PESCE [36] deduce from velocity measurements that the compressibility of such electrolyte solutions increases with the density, as the concentration varies, or almost linearly with the latter.

7. Influence of Pressure and Temperature

BIQUARD [38] continued his work on the absorption of ultrasonics in liquids by examining the effect of pressure on this factor. He likewise practises the method of light diffraction and is able to conduct the work in a chamber in which the liquid may be submitted to a pressure of 1000 kg per sq.cm. The vessel is a hollow steel cylinder nearly a metre long and 65 mm internal diameter, provided with a number of pairs of facing portholes throughout its length, through which the light beam is directed. The ultrasonic amplitude at the various stations is measured by the intensity of the light diffracted. For this a photo-electric cell is used and the light intensity at each window is assumed to bear a linear relation to the ultrasonic amplitude in question (p. 99). The end of the tube remote from the quartz emitter has jambs set at an acute angle to the axis of the tube so as to throw the reflected beam against the walls of the tube and not confound the progressive wave system in which the amplitudes are being measured. Results are given for benzene, toluene, carbon tetrachloride, methyl acetate, and water, each at one frequency and for pressures mounting up to 630 kg per sq.cm. In the liquids studied, the velocity rises nearly in linear fashion with the pressure, while the coefficient of absorption runs in the opposite sense, in accordance with the known change of viscosity with pressure (according to BRIDGMAN's results).

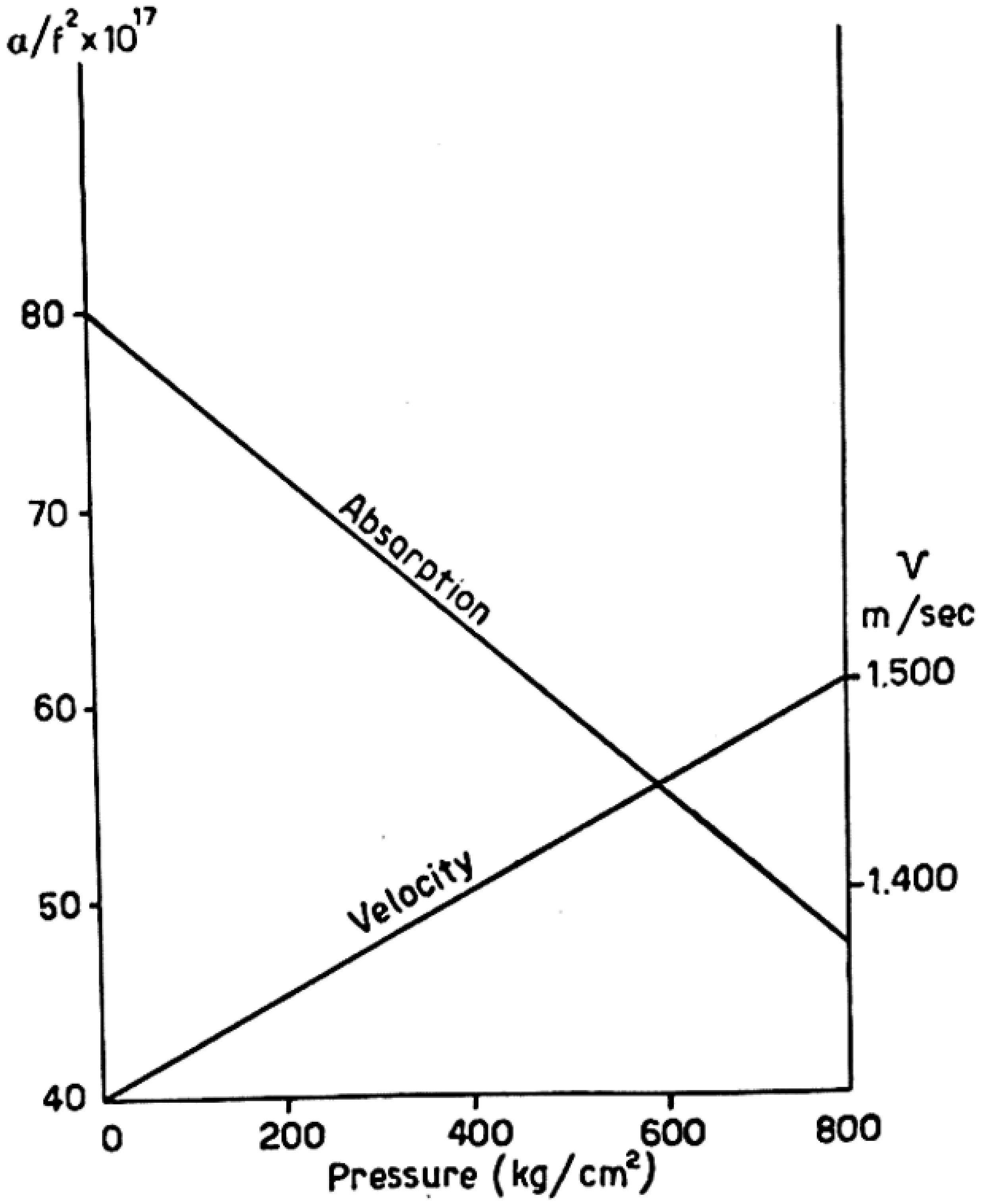

Fig. 73. Velocity and Absorption in Liquids as Function of Pressure (BIQUARD)

V increases and α decreases in linear fashion with increasing pressure until the liquid nears its point of solidification (Fig. 73). HOLTON [39] finds that water attains its classical α value at a pressure of several hundred or thousand atmospheres, depending on the temperature. At high pressures too, water is said to show no change of absorption with temperature.

8. Effect of Varying Temperature

When the temperature of a liquid is varied, interesting changes in V and a are observed. Liquids may be classified into four types in this respect.

(A) Non-polar liquids of small molecules or dipoles. These show high absorption, increasing with temperature.

(B) Liquids with hydroxyl groups, often associated.

These exhibit moderate absorption decreasing with decreasing temperature, but still greater than theory.

(C) Monatomic liquids with theoretical absorption.

(D) Very viscous liquids. The absorption is slightly greater than theory, and has a negative temperature coefficient.

The classical theory would make a/f^2 decrease with rising temperature, as the kinematic viscosity decreases. This is true of liquids in class (D) and of water. There are usually

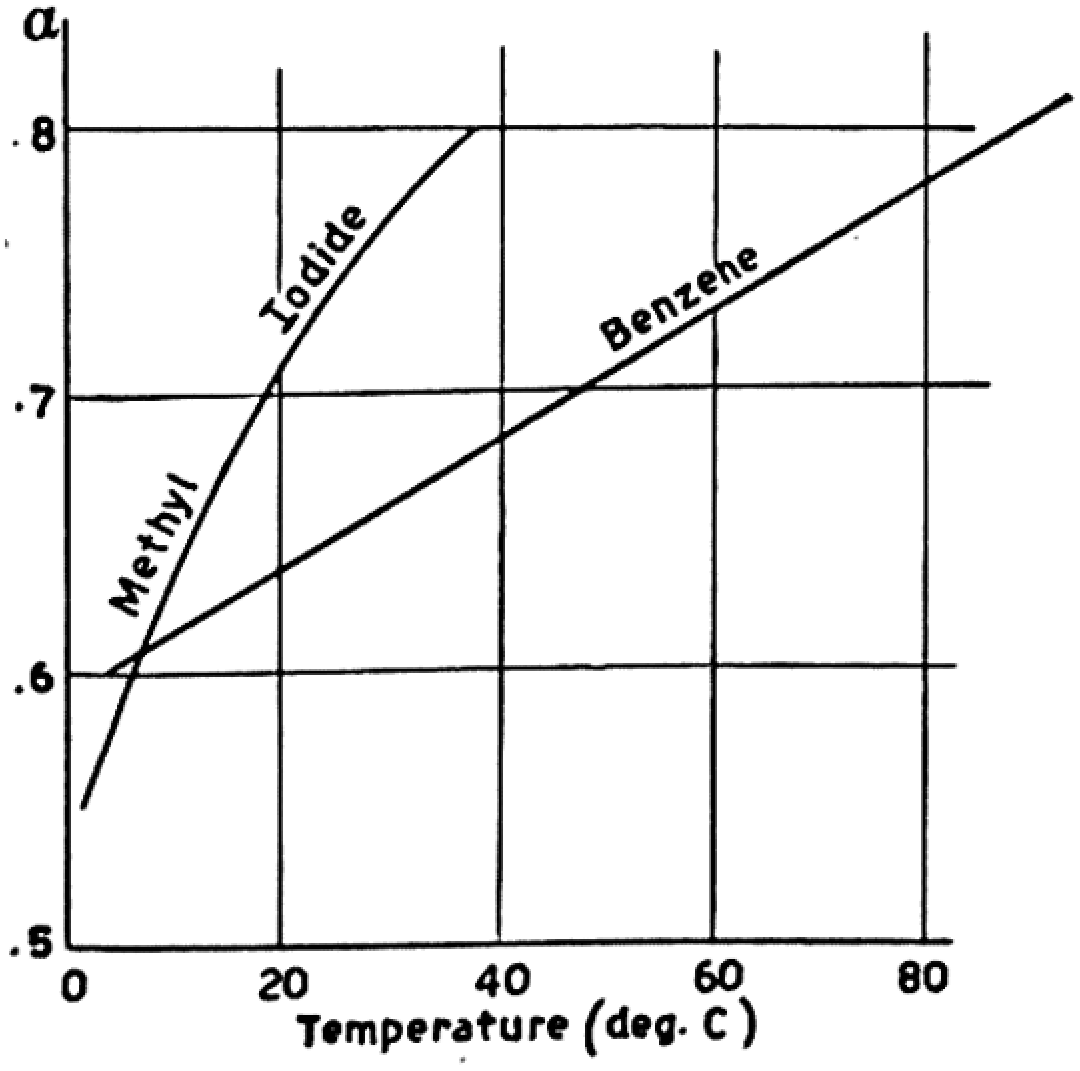

Fig. 74. Absorption Coefficient in Benzene and in Methyl Iodide as Function of Temperature

variations in the trend of absorption coefficient with temperature in the vicinity of the solidification and boiling points.

Fig. 74 gives examples of class (A) in benzene and methyl iodide. In the former the results of QUINN [40] show a linear rise of α with temperature; in the latter, the results of PELLAM and GALT [10] show a curve approaching a maximum at the boiling point.

Fig. 75 shows types which follow classical rule in exhibiting a fall of α/f^2 with rise of temperature. Of these three mercury (after RIECKMAN [6]) follows closely the Kirchhoff coefficient; so does glycerine (Class D; after

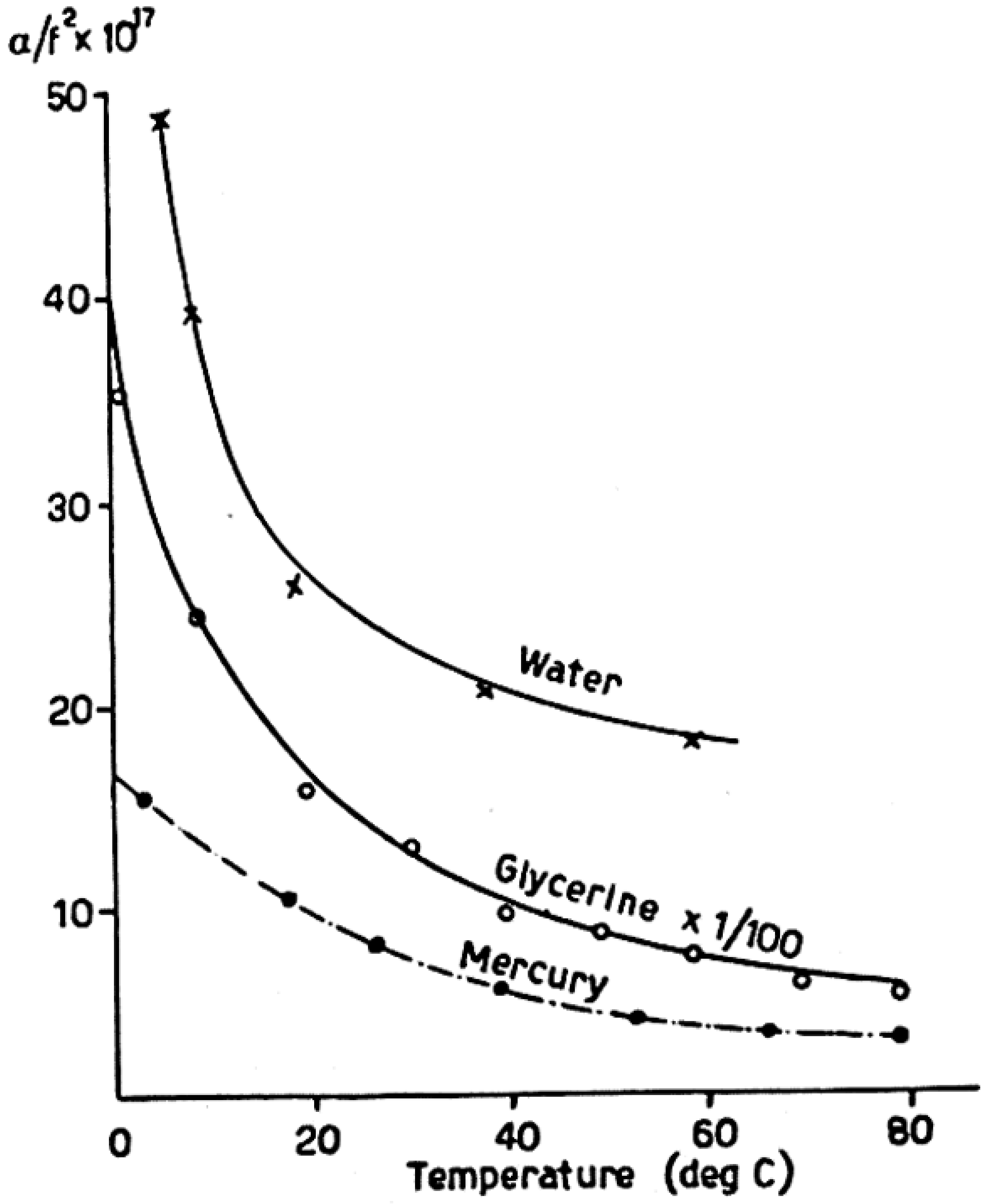

Fig. 75. Absorption in Water, Glycerine and Mercury as Function of Temperature

Hunter[41]); while water (Fox and Rock[42]) has four or five times the theoretical absorption (Class B).

Although water has been alleged to show a value for the Kirchhoff constant dependent on frequency, this results in the main from the usage of methods in the lower ultrasonic frequency range (Fig. 70) requiring large intensity. Pinkerton working between 10 Mc/sec and 70 Mc/sec, and Labaw and Williams[43] near 1 Mc/sec have failed to confirm earlier reports of peaks in α/f^2 in water, the former using pulses and the latter exploring the acoustic field in front of the source, working into a large tank of water, with a quartz microphone. Ravindranath[44] confirms an absence of dispersion of the velocity between 1 and 50 Mc/sec.

Other substances with which Pinkerton, Lamb and Huddart[30] have recently worked include acetic and propionic acids. In acetic acid α/f^2 falls with rising temperature at a low frequency (500 kc/sec) but rises in the same temperature range (16° to 60 °C) at high frequencies (4 to 60 Mc/sec). At intermediate frequencies (near 1 Mc/sec) it first rises then falls.

In propionic acid, the absorption per wave-length exhibits maxima for each frequency used; thus at 6 Mc/sec this is found at 8 °C; at 6.5 Mc/sec at 31 °C; at 7 Mc/sec, it occurs at 51 °C. The velocity is linear with temperature and not dispersed.

Giacomini[45] and his colleagues at Rome have made a number of measurements of velocity in liquid mixtures as a function of temperature. In particular he has discovered that a mixture of 17% ethyl alcohol in water has a constant velocity over the range 0° to 50 °C. More viscous mixtures show a rising characteristic with rising temperature.

9. Propagation in Condensed Gases

VAN ITTERBEEK and his colleagues [46] have made many measurements of velocity in condensed di- and monatomic gases at low temperatures, the range and nature of which are disclosed in the following table:

Condensed Gas	Range of Temperature	Range of Velocity
Oxygen	90—60 °K	910—1120 m/sec
Nitrogen	78—63 °K	875—1000
Argon	87—84 °K	840— 870
Methane	112—95 °K	1418—1545
Hydrogen	21—16 °K	1150—1300

As a function of temperature, the velocity decreases nearly in linear fashion between 60° and 90° K (at a frequency of 540 kc/sec) in liquid oxygen and nitrogen.

During the measurements in liquid hydrogen an unexpected difficulty presented itself; it was impossible to hold the velocity constant. Later this was traced to a progressive change in V during the irradiation. This, for example, is how the velocity at the boiling point, 21 °K,

Time (min)	0	15	30	35	40	45	50
V (m/sec)	1140	1170	1220	1222	1225	1230	1230

rose during the course of an experiment, eventually attaining constancy at 1260 m/sec.

The variation is ascribed to the gradual change of the normal hydrogen in the liquid mixture to the pure parahydrogen under the influence of agitation.

LIEPMAN[47] also has measured the velocity in liquid oxygen contained in a Dewar flask, the ultrasonic beam passing horizontally while the light beam passes vertically down and back upwards from a mirror in the liquid. V is linear with T over the range 90 °K to 60 °K, two frequencies; 7,500 kc/sec and 1537 kc/sec being used.

Now VAN ITTERBEEK and his colleagues are investigating absorption at low temperatures.

10. Measurement of Ionic Solvation in Electrolytes

This is a suitable point at which to refer to a theory of a possible effect of ultrasonics in sorting out ions in solution if they differ from each other in mass and charge. If this occurs it should give rise to measurable but small potential differences in the electrolyte, from which it is hoped to derive the effective mass or solvation coefficient of an ion.

DEBYE's[48] theory of this effect is somewhat akin to

EINSTEIN's theory of the dissociating gas (p. 232) as he assumes that the compressional waves can influence ionic solvation, producing a preferential motion of charges of one sign over that of ions of the other sign. Then periodically varying electric charges will accompany the sound waves. Neglecting ionic attraction, he builds up a series of equations starting with a set such as the following, one for each type of charge e_1, e_2 . . . *etc.*, in solution:

$$e_1 X - \eta\,(u_1 - U) = m_1 \dot{u}_1 \,. \tag{32}$$

Here the first term represents the electric force, the second the frictional force due to the ion acquiring a motion $\dot{u}_1$, different from that U of the main body of the liquid. If there are n_1 of these ions in solution, an equation of continuity is

$$\frac{\partial n_1}{\partial t} = \frac{\partial}{\partial x}\,(n_1 e_1) = 0 \,. \tag{33}$$

in which diffusion is neglected.

To these equations are added Poisson's equation for the whole number of ions:

$$D\,\frac{\partial X}{\partial x} = 4\,\pi\,\Sigma\, ne \,,$$

where D is the dielectric constant of the solvent.

An ultrasonic wave of velocity V, particle velocity amplitude $\bar{\xi}$ and pulsatance ω, then gives rise to an electric potential of value:

$$\varphi = \frac{m}{e}\,V\,\bar{\dot{\xi}} \cdot \frac{\sum_{1}^{j} (p_1 \zeta_1 M_1/\eta_1)}{\sum_{1}^{j} (p_1 \zeta_1^{2}/\eta_1)} \cdot \frac{4\pi K/D_\omega}{\sqrt{1 + (4\pi K/D_\omega)^2}} \,. \tag{34}$$

Here K is the specific conductivity of the solution, $p_1 \ldots p$, "fractions" of a molecule of valencies $\zeta_1 \ldots \zeta_j$, e the electronic charge, M the molecular weight of an ion, m that of the hydrogen ion.

OKA [49] allowed for relaxation but HERMANS [50] showed that OKA's correction amounted to only one per cent. He pointed out that more important terms were however wanting in DEBYE's equations. For instance, if the values for the ions are the same as that for the solvent, the expression for the potential does not become zero. HERMANS proposed the inclusion of terms dependent on the pressure gradient in the ultrasonic wave as well as others on diffusion.

BUGOSH, YEAGER and HOVORKA [51] affected the necessary modification of the equations (32) by the addition on the lefthand side of the expression:

$$-e_j\left[\frac{|e_1e_2|\,q\varkappa X}{3DBT_0\left\{1+\sqrt{q}\,(1+\iota\omega\tau)^{\frac{1}{2}}\right\}}\right]-\frac{e_jXe_0}{6\pi\eta_0 l}-$$
$$-\frac{BT}{\eta_j}\frac{\partial l^{-1}}{\partial x}+v_j\varrho_0\frac{\partial U_0}{\partial t}$$

where B is the Boltzmann constant, l the thickness of the ionic atmosphere and q for the two ionic charges is defined as

$$q=\left[\frac{e_1}{\varrho_1}-\frac{e_2}{\varrho_2}\right]\left[(e_1-e_2)\left(\frac{1}{\varrho_1}+\frac{1}{\varrho_2}\right)\right].$$

The first of these additional terms is then a relaxation with time τ; next comes the electrophoretic force, zero suffixes referring to the solvent. The third is the diffusion force and the fourth the effect of a pressure gradient $-v_j$ being the volume of the ion. Combining with equation (34) they obtain

$$\varphi = \frac{4\pi q K_0}{\omega D}\left[\frac{me_j \sum \dfrac{p_j\zeta_j M_j}{\varrho_j} - \dfrac{BT}{q^2}\sum \dfrac{p_j\zeta_j}{\varrho_j} - \varrho_0 \sum \left(\dfrac{p_j{}^2\zeta v_j}{\varrho_j}\right)}{\sum \dfrac{p_j\zeta_j{}^2}{\varrho_j}\left[\dfrac{D_{\omega}{}^2}{D} + \dfrac{4\pi}{\omega D}K_{\omega}{}^2\right]^{\frac{1}{2}}}\right]. \tag{35}$$

11. Ionic Effects in Practice

Seidl [52] showed that the electrical conductivity of liquids like hexane, toluene and carbon tetrachloride is changed when irradiated with ultrasonics. She immersed two parallel plate electrodes vertically in the liquid and sent the beam up between them. A difference of potential of 20 volts was put upon the plates and the leakage measured by a quadrant electrometer.

Adequate control had to be kept on temperature, but when this was allowed for, the radiation caused an increase in the leakage current in every case. The effect is attributed to ionic combination and breaking up of molecular complexes.

We have given above the theory of the Debye effect of ultrasonics on ionic solvation. Experimental attempts to confirm the effect are fraught with great difficulty, because the electrodes used to pickup the looked-for small alternating potential have to be set in the liquid fairly close to the ultrasonic source and so pickup much high-frequency background from the valve oscillator coupled to the source.

RUTGERS[53] first attempted to detect the effect in a colloidal suspension of silver iodide — and, later, arsenic trisulphide — using a quartz source of about 300 kc/sec. Stationary waves were set up between the source and a reflector and an electrode traversed between them. The potential on the electrode was passed to an amplifier (× 22,500). An amplitude of about 1 millivolt, owing to the DEBYE effect, was found over and above the background of 3 microvolts (when the quartz was not emitting). It will be noticed that the particle-velocity amplitude is required in equation (34). This later investigators (YEAGER, BUGOSH, HOVORKA and MCCARTHY[54]) tried to measure by means of a radiometer, but as yet there are no quantitative tests of the DEBYE and modified equations, owing to the difficulty of getting an accurate record of the ultrasonic intensity. That the effect does exist, however, seems to be established beyond doubt.

HUNTER[55] has recently proposed a pulse method and a progressive wave, absorbed at the extremity of the tank. A frequency of 465 kc/sec and a pulse duration one millisecond are to be employed. The probes will be spaced half a wave-length apart in order to get a maximum of potential difference.

12. Elastic Liquids under Shear and Compressional Vibration

Interesting are the results of the application of periodic shearing to a liquid or semi-solid which has both elasticity and viscosity. Gels and rubber solutions are examples of such visco-elastic fluids. The author[56] has experimented on cellulose acetate and gelatine sols at quite low frequencies of vibration induced by setting a horizontal plate at one end of a vertical column of such a substance into rotational motion (about its axis) of pulsatance ω.

This gives the liquid an oscillatory torque $\theta = \theta_0 e^{\iota\omega t}$ over the plate. If $\varkappa$ is the appropriate modulus of shear rigidity, η that of viscosity, the equation of motion for any annulus is

$$\ddot{\theta} = \frac{\varkappa}{\varrho}\frac{\partial^2\theta}{\partial y^2} + \frac{\eta}{\varrho}\frac{\partial^3\theta}{\partial^2 y\,\partial t} = U\frac{\partial^2\theta}{\partial y^2} + \nu\frac{\partial^3\theta}{\partial^2 y\,\partial t} \tag{36}$$

U being the velocity of the shear waves. The amplitude at any level y, in terms of that at the plate, is given by equation (13'), p. 72.

$$\theta_y^2 = 2\theta_0^2\left[\cosh\left\{2\alpha(y-l)\right\} - \cos\left\{2\beta(y-l)\right\}\right]. \tag{37}$$

Substituting (37) in (36), we derive

$$(\alpha^2 - \beta^2 U^2)(U^4 + \nu^2\omega^2) = -\,\omega^2 U^2$$

$$2\alpha\beta\,(U^4 + \nu^2\omega^2) = -\,\nu\omega^2$$

$$\frac{\alpha^2}{\omega^2} = \frac{\sqrt{U^4 + \nu^2\omega^2} - U^2}{2\,(U^4 + \nu^2\omega^2)} \tag{38a}$$

$$\frac{\beta^2}{\omega^2} = \frac{\sqrt{U^4 + \nu^2\omega^2} + U^2}{2\,(U^4 + \nu^2\omega^2)} \tag{38b}$$

Note that when $\nu = 0$, $\alpha = 0$ and $\beta = \omega/U$: when $\varkappa = 0$:

$$\alpha = \beta = \sqrt{\omega/2\nu} \tag{38c}$$

(*cf.* p. 203).

In general, if the velocity amplitude is measured (by hot-wire) at various levels over the oscillating plate, the liquid is found to exhibit pseudo-nodes and antinodes like those of a column of absorbent fluid in *longitudinal* vibration (p. 72). Typical values of relaxation time are: 4% viscose, 0.004 sec; 10% gelatine sol, 0.01 sec; hexane 7 parts and methanol 3 parts, 0.7 sec; all at room temperature.

This method of the oscillating plate is, of course, only suited to audio frequencies. Many liquids of this type have relaxation times which need to be pursued into ultrasonic

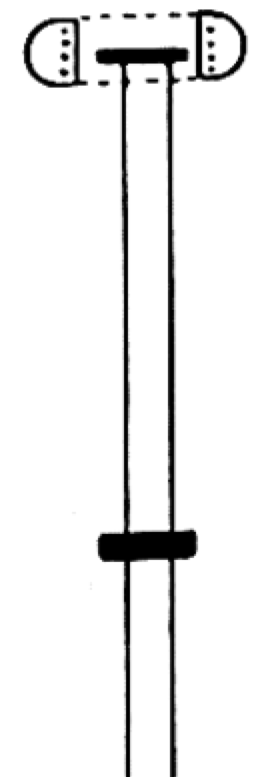

Fig. 76. Apparatus for Studying Shear Waves in Liquids

time-periods. For these, a number of methods are available.

A metal rod (Fig. 76) several feet in length may be clamped in a vertical position at its mid-point, while a steel peg or cross-piece attached at its upper end projects into the field of an electro-magnet whose coil is so wound that when an alternating current from a powerful valve oscillator at the requisite frequency is fed into the coil, the peg is set into forced angular motion about the axis of the rod. When the frequency of the applied field is adjusted to one of the natural torsional modes of vibration of the rod, the latter responds. As its lower end dips into a trough containing the liquid under observation, it sets up shear waves in the latter. These will be stationary waves if the interspace between rod and cylindrical wall of the vessel is also suitably adjusted so that it is a multiple of the wave-length in the liquid in accordance with equations of the analysis below. The equation of motion for this case, in which the waves are propagated radially, is:

$$\ddot{\theta} = U^2 \left(\frac{\partial^2 \theta}{\partial r^2} + \frac{3}{r} \frac{\partial \theta}{\partial r} \right) + \nu \left(\frac{\partial^3 \theta}{\partial r^2 \, \partial t} + \frac{3}{r} \cdot \frac{\partial^2 \theta}{\partial r \, \partial t} \right) \quad (39)$$

corresponding to (36) in the case of the column of fluid. If in this we substitute $\theta = \psi e^{\iota \omega t}$, ψ being a function of r alone,

$$\frac{\partial^2 \psi}{\partial r^2} + \frac{3}{r} \cdot \frac{\partial \psi}{\partial r} + (\alpha - i\beta)^2 \, \psi = 0 \, . \quad (40)$$

The solution of this is obtained in terms of Bessel functions of complex argument, as

$$\psi = [J_1 r(\alpha - i\beta)]/[r(\alpha - i\beta)] \,. \qquad (41)$$

(Those functions for $\alpha = 0$ and $\alpha = \beta$ can be obtained from tables of the Bessel functions, while the others for integral values of α and β lend themselves to calculation from a reduction formula or are available in the Smithsonian Tables.)

On Fig. 77 are shown typical plots obtained with the hot-wire exploring shear waves set up in gelatine solution in the bowl at audio-frequencies. In the ultrasonic gamut, the shear waves are rapidly attenuated and do not penetrate far into the liquid.

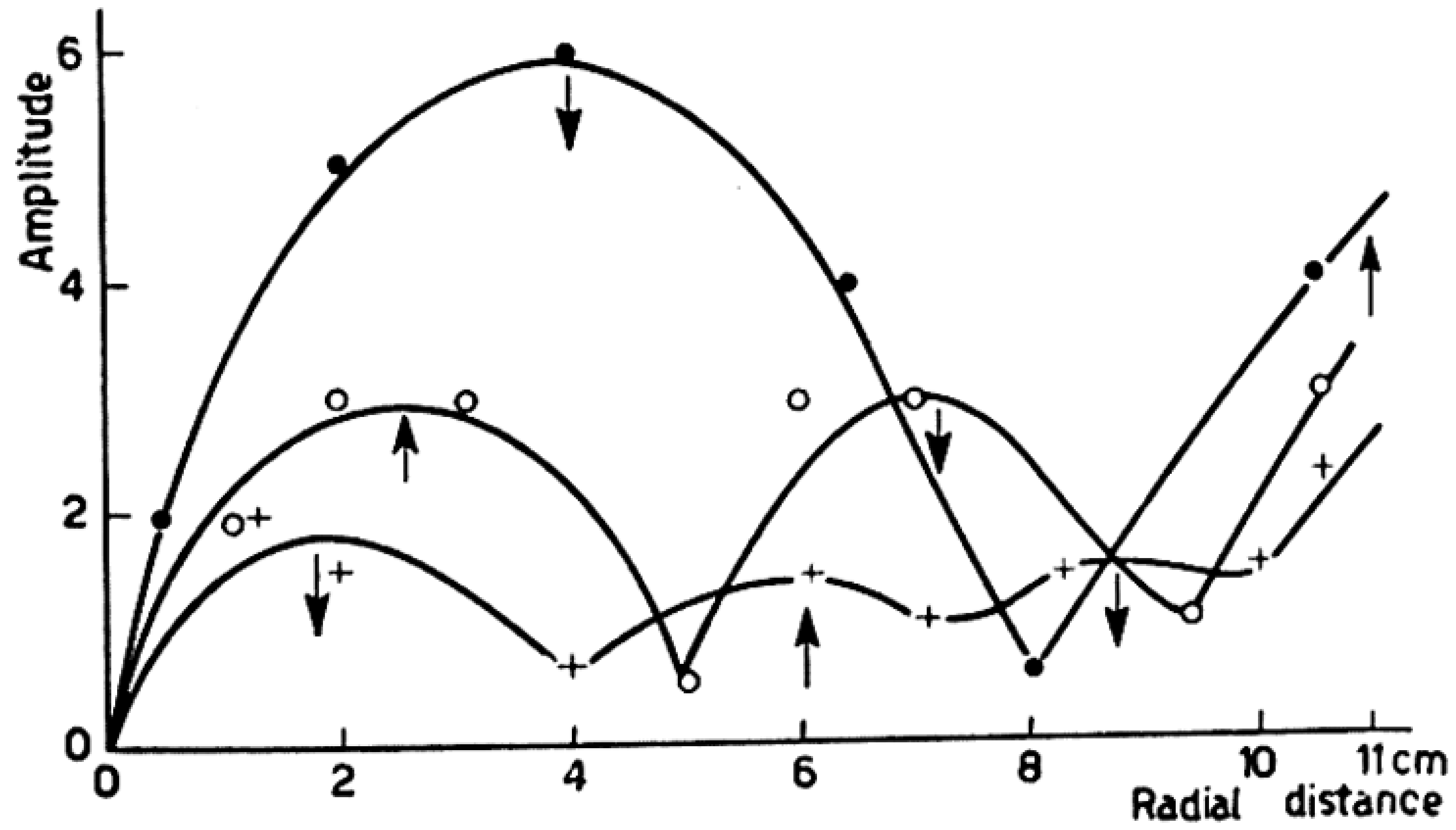

Fig. 77. Results in 3% Gelatine Sol

Since ω is then dependent on U, r and a for the setting up of a stationary wave pattern in the liquid, whereas in the rod it is limited to the natural torsional modes, some means of synchronising frequencies is needed, of which probably the simplest is to increase the inertia of the rod by collars fixed one at each end symmetrically to the mid-point but with the lower one clear of the liquid. Once the existence of stationary waves has been established, by watching the motion of the surface, the velocity amplitudes in the pseudo-nodes may be explored with a hot-wire detector. The results of such an investigation in a polymer solution have been carried up to a frequency of 10 kc/sec.

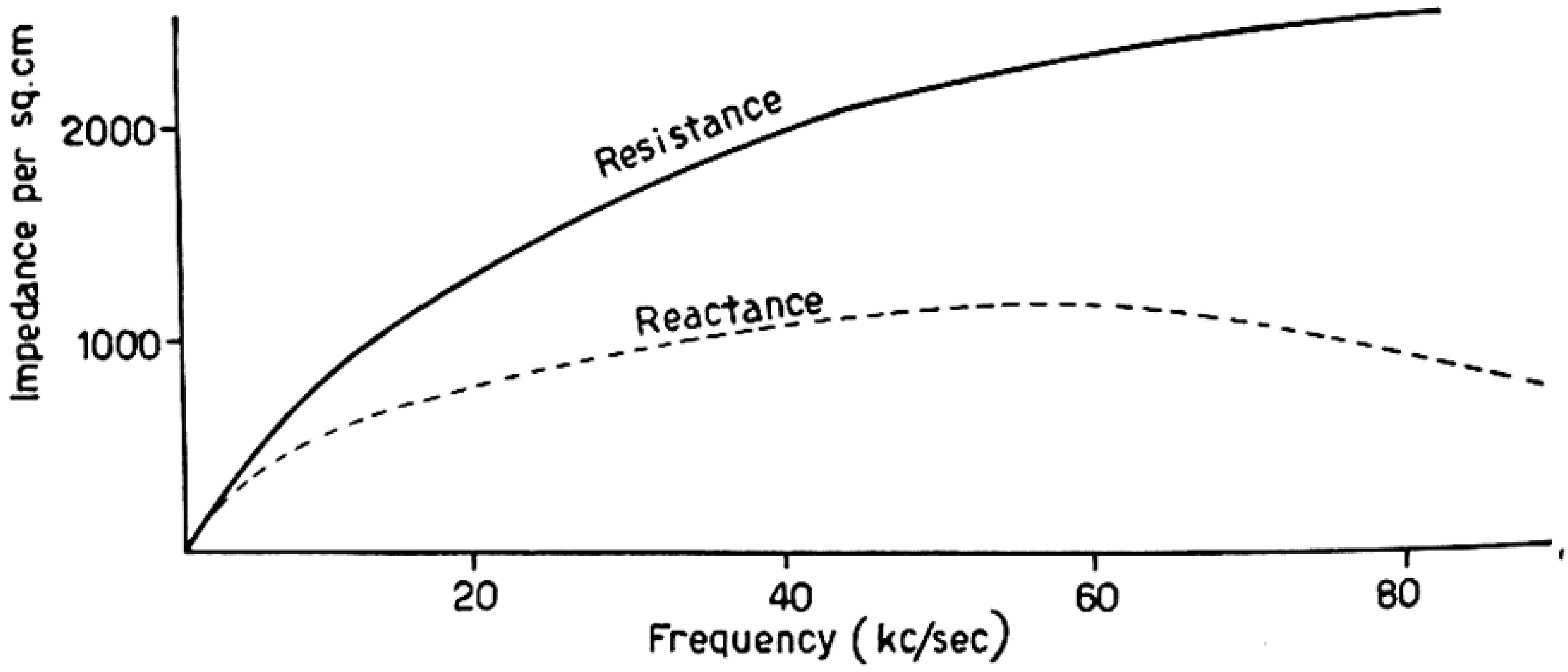

Fig. 78. Impedance of Visco-Elastic Fluid at Various Frequencies (MASON)

These liquids can, in fact, be regarded as possessing a complex impedance Z of which $\alpha + i\beta$ (*vide supra*) is the indicator. Writing $Z = R + iX$, in which R is the resistive and X the reactive component, we can derive from equations such as (38) values of R and X appropriate to the material. Such (after MASON and MCSKIMIN[57]) are exhibited on Fig. 78 as functions of frequency. They consider that the effect of a shear can be represented as the action of a compliance in parallel with a viscous resistance, which is a branch upon a line containing reactance (Fig. 79). At low frequencies the liquid behaves in flow as a viscous liquid, but at sufficiently high frequencies, a movement of one part of it is transmitted as a shear wave.

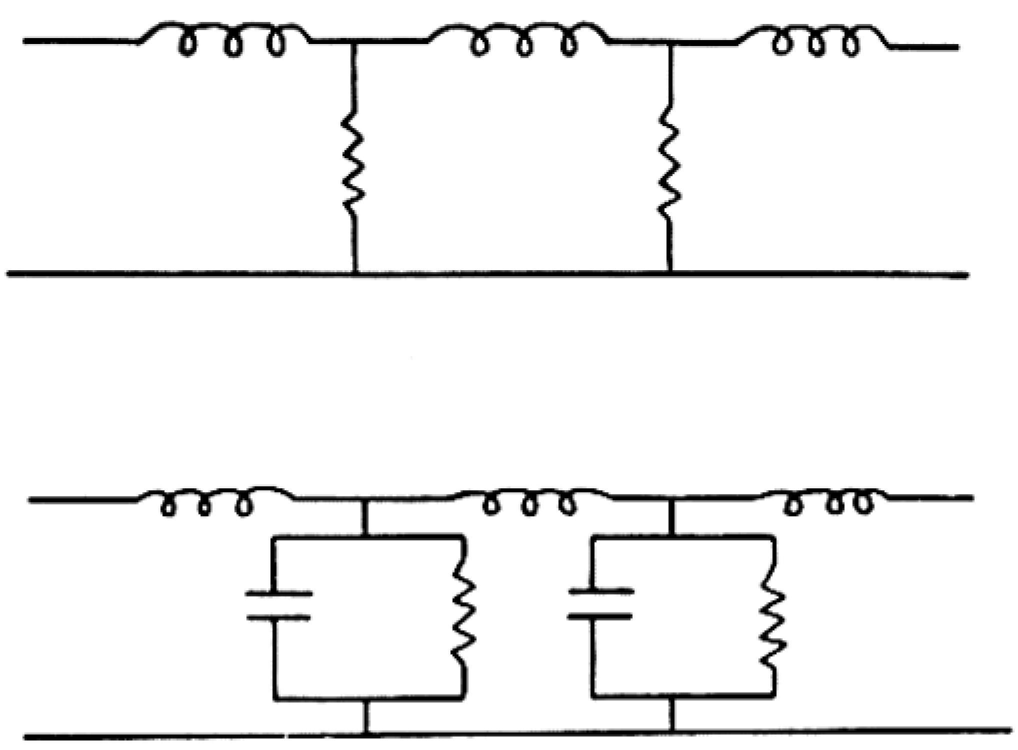

Fig. 79. Equivalent Electric Lines of (a) Viscous Medium (b) Medium with Shear Elasticity

The propagation constant is $\alpha + i\beta$ and the characteristic impedance of the "line" is obtained in terms of equations (34) by multiplying the appropriate propagation constant by the density. In terms of the line impedance (Z_1) and the shunt impedance (Z_2) of Fig. 78, the quantities which intervene in the propagation constant are respectively $\sqrt{Z_1/Z_2}$ and $\sqrt{Z_1 Z_2}$.

In very viscous liquids the methods of the author (*vide supra*) would fail as the attenuation of shear waves would be too great for the setting up of any form of stationary vibration in the trough of liquid. MASON [58], however, by measuring the load on a torsional piezo-electric generator (p. 10) immersed in such a liquid, imposed by its visco-elastic properties, is able to measure this twofold property indirectly. At frequencies of the order of 10 to 150 kc/sec, liquids usually regarded as purely viscous are forced to disclose their latent shear elasticity. Thus, solutions of polybutylenes and polystyrenes have a shear stiffness of the order of $3 \cdot 10^7$ dynes/cm² in the neighbourhood of 300 kc/sec but this rises to $5 \cdot 10^9$ in the megacycle range. Both resistive and reactive components of the stiffness increase with molecular weight in a homologous series and decrease with rising temperature. It is assumed that this complex viscosity arises from the dislocation of molecular chains from which the molecule can recover at low but not at high frequencies of agitation.

In the practice of MASON's [58] experiments with torsional generators, it is found that the crystal tends to perform some flexural vibration, *e.g.*, with one diameter of the cylinder expanding while another contracts. If while the crystal is in air it be surrounded by a coaxial metal shield, longitudinal waves will be radiated towards the shield by this unwanted type of vibration. At frequencies below that at which longitudinal stationary waves can be set up in the interspace, the additional load on the generator due to this radiation will be purely resistive. This amount may be measured as the difference, if any, between values of the resistance with and without the shield in place.

Another test of the presence of longitudinal radiation which MASON made was to vary the pressure of a gas (nitrogen) surrounding the crystal. As a gas has no rigidity, the loads afforded by it when radiating shear waves are proportional to $\sqrt{\varrho}$ at a fixed frequency (*cf.* p. 193) and so to $\sqrt{p}$, whereas those owing to longitudinal radiation are proportional to ϱ and so to p.

Finally a crystal and mounting were selected for which departures from ideal loading of purely torsional vibration were small. Noting the results of Fig. 78, we observe that, in agreement with theory, the two components of load conspire at low frequencies but diverge as the reactance falls off towards zero and the resistance rises towards a constant value at higher frequencies. In effect the shear elasticity then "shunts out" the viscous component and thereby reduces the attenuation.

Whenever pseudo-stationary waves of the type already demonstrated are set up, as the driving frequency is varied, these resonances become apparent in MASON's apparatus as peaks in the crystal impedance.

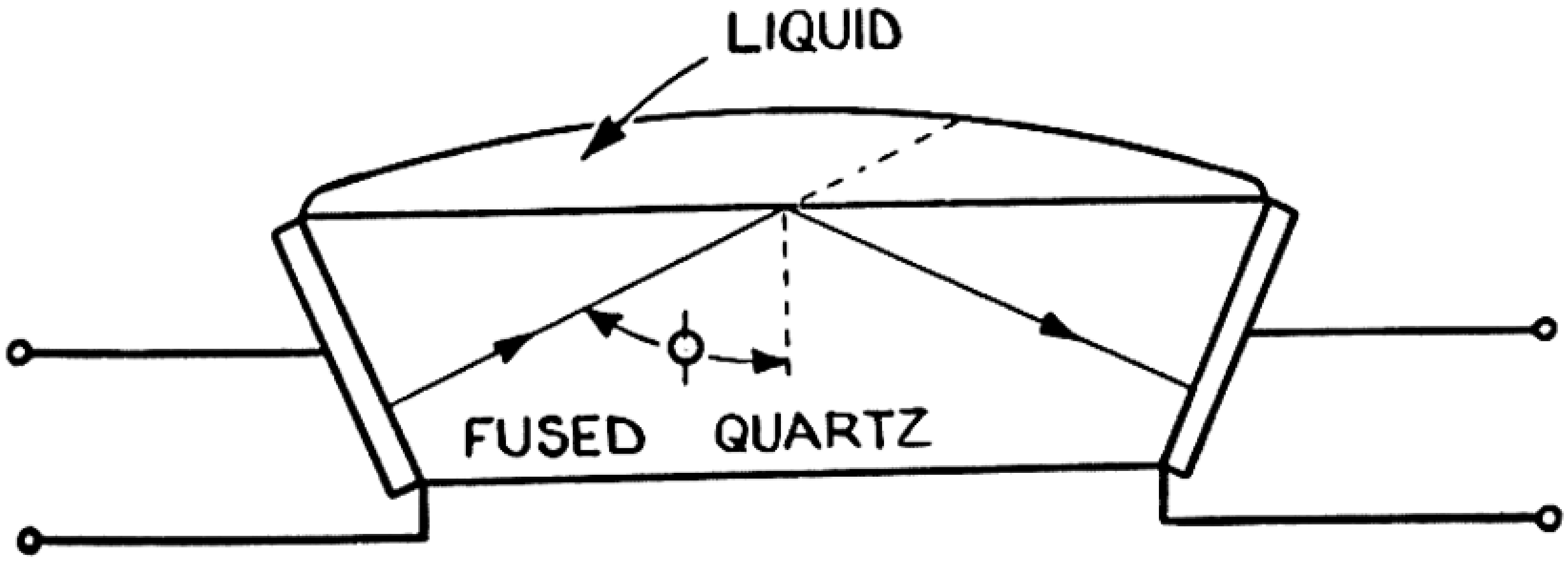

Fig. 80. High Frequency Shear Wave Generator for Liquids (MASON)

For frequencies above ½ Mc/sec, MASON and his colleagues replace this method by one in which shear waves are set up in a fused quartz rod through the intermediary of a Y-cut crystal soldered by a layer of baked silver paste to one bevelled face (Fig. 80). A similar crystal on an opposite jamb of the fused quartz block conveys the signal received by reflection from the top (horizontal) face. When a liquid is placed on the top surface, there is a change in the amplitude and phase of the emitted pulse when picked up at the receiver. These are compared with the signal transmitted through a duplicate quartz which carries no liquid film.

MASON [58] has used in this apparatus solutions of poly*iso*butylene. The shear elasticity is directly proportional to the concentration of solute (as the present author [56] found in solutions of viscose in acetone). The viscosity, however, rises with concentration rapidly, an effect which MASON ascribes to the ravelling of cyclic chains in the polymer molecule. The apparent stiffness decreases with rise of temperature, the frequency remaining constant the while, but if the latter is varied there is a rather complicated variation of stiffness. In the poly*iso*butylene solutions relaxation frequencies of about 500 c/sec, 80 kc/sec, and 4 Mc/sec are indicated. Measurements on a series of polymer solutions showed the shear elasticity to be proportional to chain length.

When data on pure *iso*butylene liquids of varying molecular weight were compared, two relaxation ranges were disclosed of which the upper — in the megacycle range — was taken to indicate the onset of crystalline elasticity in the liquid, *i.e.*, the region of frequency for which the shortest chain segment cannot move within the time-period of a single cycle.

It is, of course, possible to find liquids or semi-solids which show a similar interaction between viscosity and either bulk or Young's modules of elasticity when transmitting compressional waves. According to MAXWELL [59] all liquids possess the two properties, bulk elasticity and viscosity, interelated by a relaxation time τ, so that $\eta/\tau = E$. (We shall elaborate MAXWELL's idea, insofar as it applies to our problems, in Chap. VII).

The equation for plane compressional waves is formally similar to (32) with E replacing $\varkappa$, and we may show from (33) that such a liquid in a moving reflector interferometer has peaks for values of l satisfying

$$\alpha \tanh \alpha l = -\beta \tan \beta l \,. \tag{42}$$

SCHALLAMACH [60] has studied organic liquids and MIKHAILOV and GUREVICH [61] rosins from this aspect. Whereas in ordinary liquids, no elastic effect on velocity is apparent, the quasi-solids, rubbers and rosins, show a rising velocity with frequency and a maximum attenuation which varies with frequency. The effective modulus and attenuation (for compressional waves) as a function of frequency in rubber at three temperatures are shown later in Fig. 90. In highly viscous rosin and in methyl methacrylate, the Russians find no peak of absorption but a steady rise with the square root of the frequency, indicating no relaxation.

In all these substances the elastic modulus falls with increasing temperature.

13. Velocity in Liquid Helium

We complete this chapter by discussing a subject which, though strictly more concerned with sonic vibrations, has become in theory and practice closely bound up with ultrasonic aspects.

When helium is liquefied at its normal boiling point (4 °K) and further cooled there is a transformation into another helium (I → II) near the so-called λ point (2.2 °K). If one tries to measure the velocity or absorption of sound in liquid helium as its temperature is lowered, as PELLAM and SQUIRE [63] have done, there is found an ambiguity at this point as Helium I is gradually transformed into Helium II and a different trend in the velocity below this temperature (Fig. 81).

Helium II has peculiar properties, notably very low

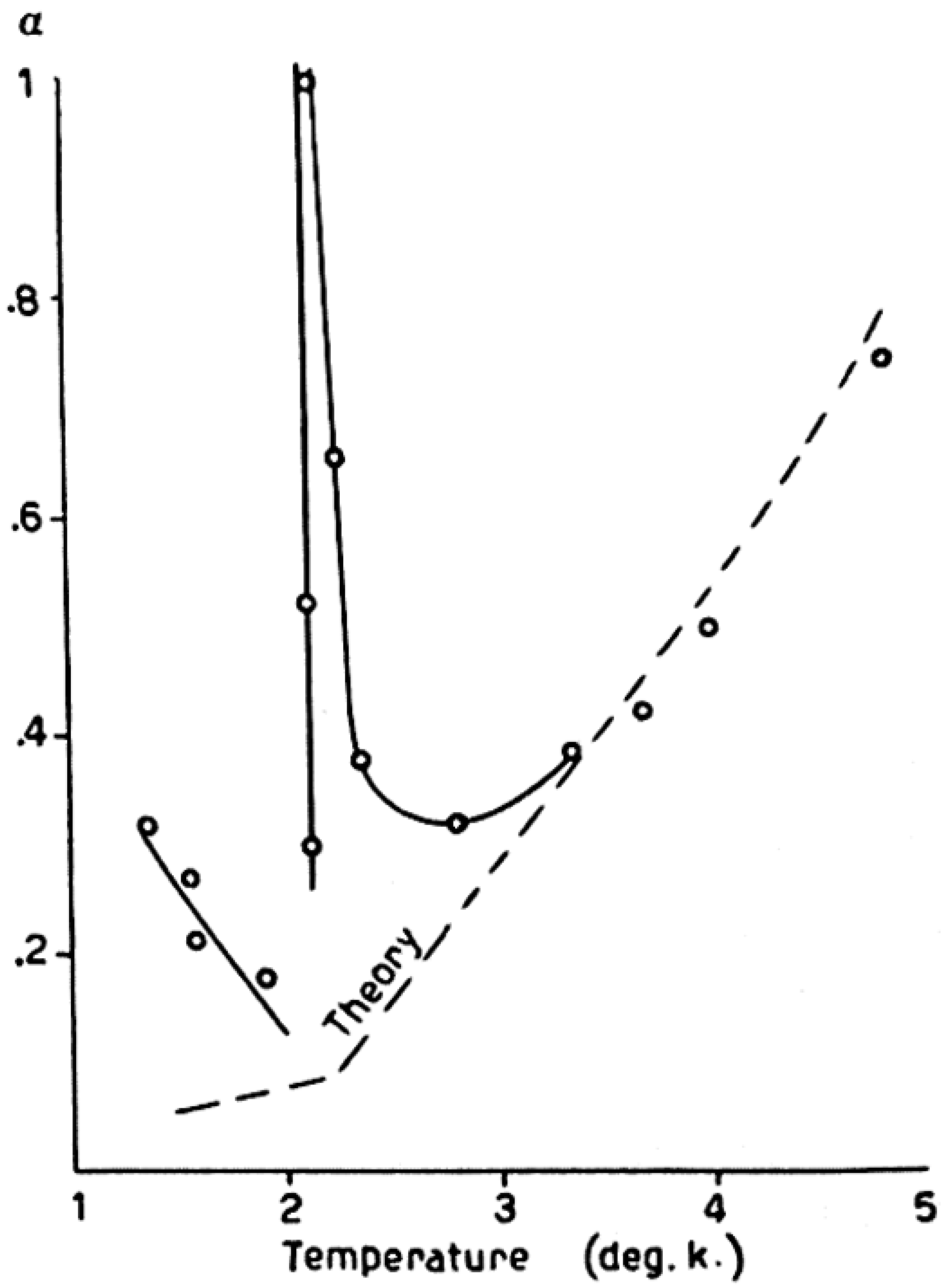

Fig. 81. Absorption Coefficient of Liquid Helium (PELLAM and SQUIRE)

viscosity ("superfluidity"), and a high rate of thermal transmission ("supraconductivity"). The first leads to a very mild attenuation of sound, the latter to the capability of transmitting thermal waves to a considerable distance without loss. It is, in fact, possible to use two different kinds of source in this strange liquid, (1) an ordinary electro-mechanical transducer such as a diaphragm or ultrasonic crystal, giving rise to "first sound"; (2) a thermophone giving rise to undamped thermal waves, or "second sound" as the Russians call it. Furthermore, owing to supraconductivity, the normal sound is likely to be transmitted at the isothermal velocity — treating the substance as a condensed gas — $\sqrt{p/\varrho}$ instead of $\sqrt{\gamma p/\varrho}$ as adiabatic conditions cannot be maintained. (In fact, this is a distinction without difference as the appropriate value of γ is unity.)

The thermophone is a metal strip of platinum to which an alternating current of pulsatance ω is applied. This makes the fluid in its vicinity undergo a periodic heating and cooling of amplitude T_0. This is propagated outwards as a nearly plane progressive wave of amplitude T_x at any distance x perpendicular to the strip

$$T_x = T_0 e^{-ax} \sin (2\omega t - ax) \,. \qquad (43)$$

It can be shown that the attenuation factor is given by $\sqrt{\omega/2k}$ where k is the thermal diffusivity of the fluid, and the velocity by $\sqrt{2\omega k}$, the wave-length being $\sqrt{8\pi^2 k/\omega}$. In an ordinary fluid, the strip when supplied by a.c. sends out such waves of double the applied frequency but they are rapidly damped; together with these it sends out sound waves owing to the local expansions and contractions of the fluid. In Helium II however the latter might be expected to fail, owing to the difficulty of locally heating a medium of such high conductivity, whereas the former can persist for quite a distance.

Peshkov[64] made experiments with a thermophone source in liquid helium near the λ-point and used a resistance

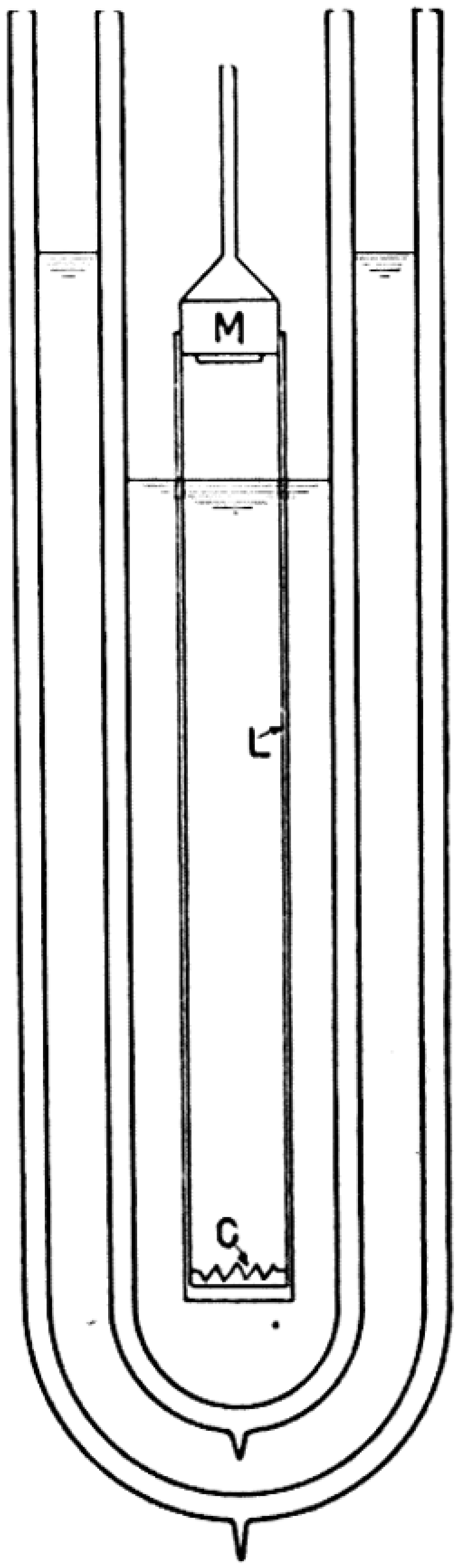

Fig. 82. Apparatus for Velocity of Second Sound in Helium II (Lane and Fairbank)

thermometer to plot out the stationary thermal waves set up between the hot source, radiating vertically, and the free surface of the liquid. His results indicate a thermal diffusivity for this fluid of order 10^3. H. A. and W. M. LANE, and FAIRBANK [65] have made similar measurements in a Dewar vessel, letting the arrival of the thermal waves at the free surface produce fluctuations in the vapour above which could be recorded on a microphone. It occurred to them that it might be possible to generate second sound at a liquid-vapour interface by generating normal sound in the vapour to be reflected at the interface. The consequent pressure fluctuations should give rise to second sound waves in the liquid. Fig. 82 is a sketch of their apparatus. The lucite tube L is closed at one end by a microphone M and at the other by a carbon strip resistance thermometer as detector, C. When sound of frequency 1000 c/sec came from the transmitter into the helium, the output of the detector C was amplified, rectified and recorded on a recording potentiometer. The length of the liquid column remained substantially constant during this temperature sweep, and a resonance peak occurred whenever the velocity was such that the liquid column was an integral number of half-wave lengths of thermal waves. They found that the resonances came successively closer together and finally disappeared at the λ-point. This allowed calculation of the velocity of second sound at a series of temperatures and the results were in substantial agreement with those of PESHKOV.

Liquid	20 °C V m/sec	α per cm 1 Mc/sec	α per cm 10 Mc/sec	$\alpha/f^2 \cdot 10^{15}$ Expt.	$\alpha/f^2 \cdot 10^{15}$ Theory	Temperature Range °C	Freq. Range Mc/sec	Range of Pressure	Note page
Water	1440	0.001	0.04	0.5	0.08	0 to 80	0.1 to 200	1 to 6000	177
Acetone	1170	0.001	0.02	0.6	0.07	18 ,, 40	0.2 ,, 54		179
Chloroform	995	(0.01)	0.4	2	0.12		2 ,, 16	1 ,, 300	
Bromoform	900		0.25	2.3			7 ,, 10		
Carbon tetrachloride	930	0.006	0.6	4			0.2 ,, 105	1 ,, 300	
Carbon disulphide		0.03	3	50	0.05		0.2 ,, 105	1 ,, 300	
Benzene	1250	0.005	0.7	8	0.09	7 ,, 80	0.2 ,, 165	1 ,, 300	183
Toluene	1300	0.005	0.09	1	0.08	13 ,, 25	0.4 ,, 75	1 ,, 6000	
Xylene	1325	0.005	0.08	0.7	0.08		0.4 ,, 16		
Chlorbenzene	1333		0.18	1.7	0.1		3 ,, 30		
Nitrobenzene	1490		0.09	0.8	0.16	7 ,, 23	6 ,, 15		
Acetic acid	1150	0.04	1	12	0.17	15 ,, 60	0.5 ,, 70		185
Methyl acetate		0.011	0.09	0.8	0.07		0.8 ,, 70	1 ,, 6000	
Ethyl acetate	1145		0.07	0.6	0.08		3 ,, 70		
Amyl acetate	1170	(0.0015)	0.02	0.4			2.5 ,, 70		
Formic acid			0.02	2			4 ,, 10		
Ethyl formate	1260	—	0.08	0.7	0.07		3 ,, 16		
Methyl alcohol	1120		0.08	0.9	0.14		7 ,, 250		176
Ethyl alcohol	1150	(0.016)	0.1	0.4	0.3		0.2 ,, 220		

Amyl alcohol	1225		0.09	1	0.64		3 ,, 16		
Propyl alcohol	1200		0.075	0.7	0.3		3 ,, 16		
Dibromethylene	932		(.07)	0.7	0.1	2 to 30	15		
Dichlorethylene	1108								
Dichloracetylene	1025		0.4	4			6 ,, 10		
Methyl cyanide	1280		0.08	0.8			6 ,, 10		
Chlorbutyl	(1213)		(0.1)	1.1	0.1		15		183
Hexane (cyclo)	1250	0.0006	0.23	2	0.1		0.7 ,, 25		
Hexane (normal)	1085		0.07	0.8	0.1		3 ,, 16		
Ethyl ether	985		0.15	0.4	0.09		8 ,, 40	1 to 6000	
Formamide	1610		0.06	0.6			10		
Methyl iodide	840		(0.3)	3	0.1	2 to 40	15		183
*Iso*pentane	985		0.16	1.6			10		
Tetraline	1465		0.02	0.6	0.18		3 to 16		
Kerotine	1315		0.12	1.1			6 ,, 20		
Butylene glycol			2.1	20			6 ,, 10		
Glycerine	1910	0.022	2.3	30			0.2 ,, 7		184
Mercury			0.006	0.065	0.055		6 ,, 54		184
Oxygen	1120 to 910		(0.009)	0.09		60 °K to 90 °K	7 ,, 44		186
Nitrogen	1200 ,, 875		(0.011)	0.10		55 °K ,, 18 °K	0.5 ,, 45		186
Hydrogen	1340 ,, 1150		(0.006)	0.06		14 °K ,, 21 °K	0.5 ,, 44		186
Argon	873 ,, 840		(0.01)	0.10		81 °K ,, 85 °K			186
Helium I	230 ,, 175			2.3		1.6 °K ,, 5 °K	15		202

The velocity is found to be zero at the λ-point, reaches a maximum of 20 m/sec at 1.7 °K and decreases thereafter at still lower temperatures (Fig. 83).

PELLAM[66] has been able to initiate pulses of the second sound by applying d.c. for a short time to the thermophone, picking up the thermal wave on its arrival at the resistance element. By moving source and receiver relative to each other the attenuation in Helium II can be calculated as well as the velocity. The presence of first sound in the wave from the thermophone was shown by its ability to affect a vibration microphone placed in its path.

The question of the "conversion of second into first sound" is subject to a certain amount of confusion. It is sometimes overlooked (a) that the thermophone in a normal fluid produces "first sound" waves, the pressure amplitude arising from local expansions and contractions, (b)

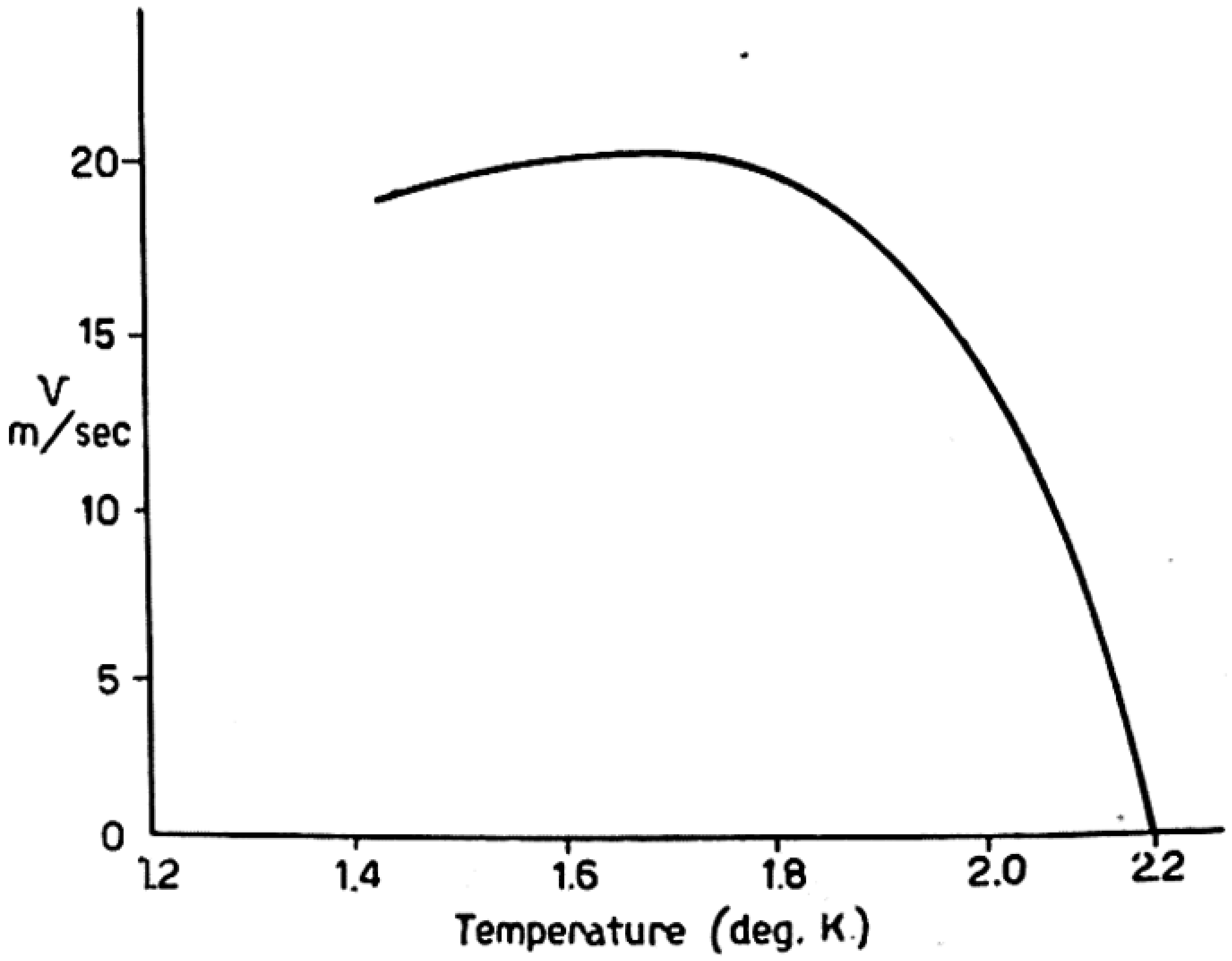

Fig. 83. Variation of Velocity with Temperature in Liquid Helium

that a resistance element is a well-known detector of ordinary sound as well as of thermal waves. It appears to the writer therefore that the origin these so-called "conversions" may be looked for in the nature of the sources and detectors employed.

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SOLUTIONS OF NON-ELECTROLYTES

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CHAPTER VI

PROPAGATION IN SOLIDS

1. Plates

Boyle and his colleagues in Canada made the earliest measurements on the transmission of ultrasonics through solids in the form of plates in the First World War, though the work was covered by a veil of secrecy until several years later. Incidentally, they established the formula (3) of p. 36 for the ratio of incident to reflected energy of a plate suspended in a liquid to act as a torsion vane.

At normal incidence, the transmission is a minimum for

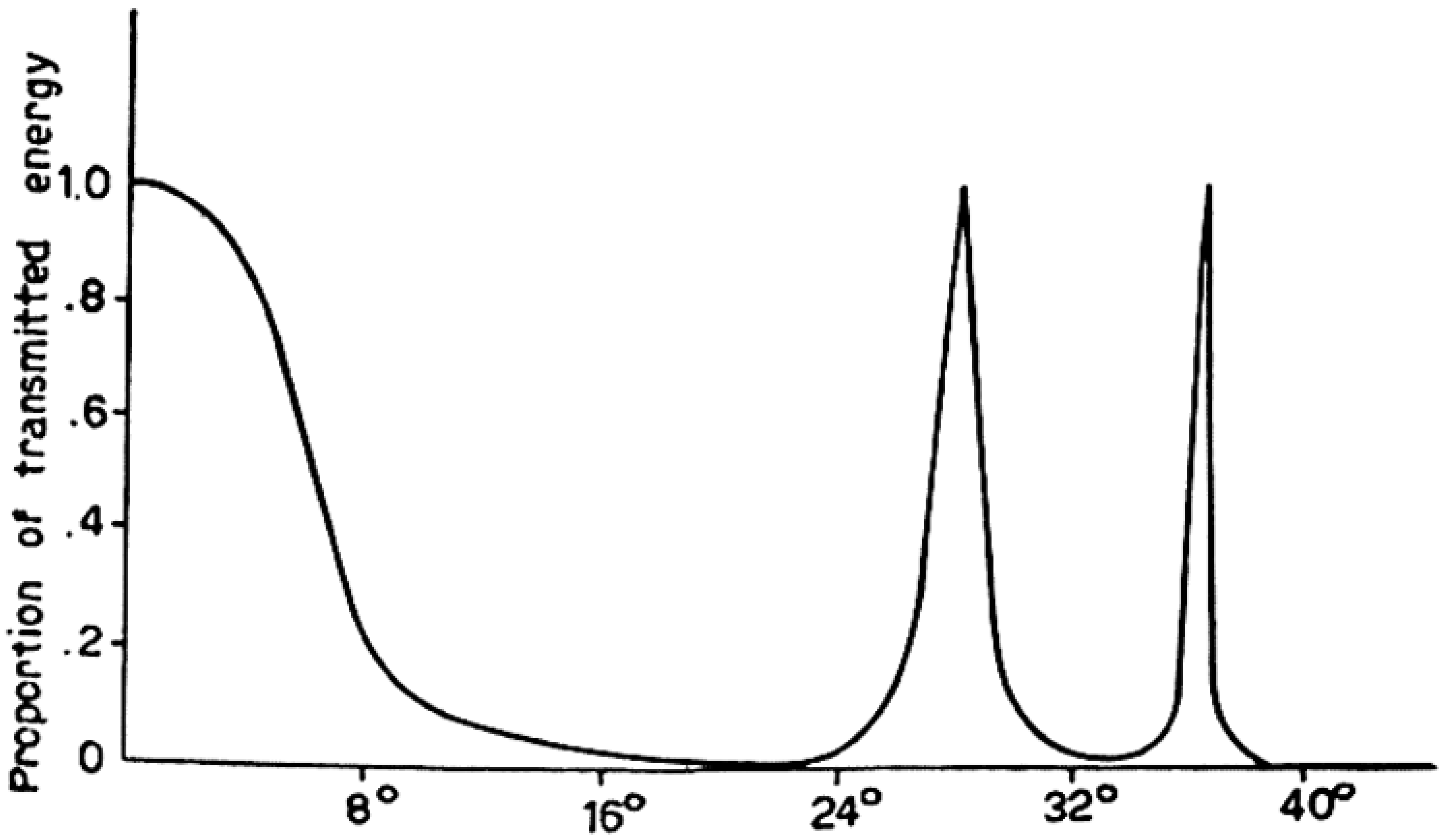

Fig. 84. Transmission of Ultrasonics in Metal Plate as Function of Incident Angle (Boyle and Rawlinson)

References pp. 230–231

a quarter wave-plate. Such measurements of reflected and transmitted energy permit of the velocity in the solid being calculated (BOYLE and LEHMANN [1]; BOYLE and SPROULE [2]). Alternatively if the thickness of the plate and frequency are invariable and the plate inclined to the incident beam, a minimum of reflection will be found whenever the distance to be traversed in line of beam is a multiple of a half wave-length (*cf.* Fig. 84, after BOYLE and RAWLINSON [3]).

2. Propagation in Rods

Latterly, there has been more interest in the propagation in solid rods. BOYLE and SPROULE started this with their rods submerged in water, looking for resonance in length to applied frequency by the cavitation in the surrounding liquid, by the formation of dust figures on the top, by a form of stethoscope or by reaction on the driving circuit.

At sufficiently high frequencies, they detected radial modes of oscillation which react on the velocity of longitudinal modes, in the same fashion as those we have noted in columns of gas (p. 81). The observed curves connecting velocity with frequency are, as theory [4] would have, nearly parabolic, except when resonance between longitudinal and radial waves ensues.

RUEDY [5] also drew attention to the coupling between longitudinal and radial modes, with the consequent lowering of the speed of transmission along the rod as the frequency goes up. The velocity, as in a fluid in a tube, will, in fact, only agree with that of the elementary formula for low frequencies in narrow rods. He envisages also the scattering of the radiation by grains or crystals in the structure, later discovered in experiments by ROTH and by MASON and McSKIMIN (*vide infra*).

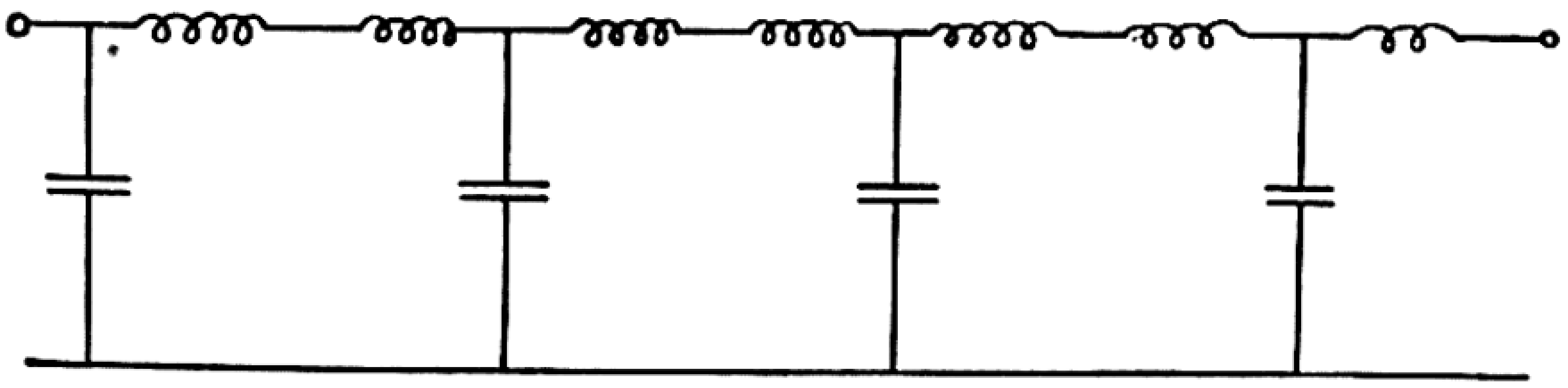

Fig. 85. Electric Transmission Line, Analogue of Rod

Fig. 85 (after BRADFIELD) shows the electrical analogue of a rod. It is a line where part of the main velocity is shunted into branches corresponding to the radial motion of the rod. When the branch resonates as the frequency is raised, discontinuities in the phase velocity are observed corresponding to those in the rod when a radial mode is in resonance. It is clear, then, that the rod can act as a filter.

MORSE[7] calculated the velocity of compressional waves in bars of rectangular cross-section and checked his results with experiments. In a bar of wafer type having width comparable with the length but a much smaller thickness — a type he has studied too — there is a dispersion of the velocity and a cut-off frequency for which the half wavelength (in an infinitely wide slab) is equal to the actual width of the bar.

There is also a dispersion of the thickness mode, and the

References pp. 230–231

velocities can be expressed in terms of an "aspect ratio" (of thickness to width). The measurements were made by exciting the vibrations of brass plates by contact with a quartz crystal (mounted in a liquid), in a modification of the RÖHRICH [8] technique (*vide infra*). The crystal could thus be driven at frequencies ranging from 200 to 650 kc/sec and the modes of the bar determined from the CHLADNI figures of lycopodium powder strewn over its surface.

A number of other methods for solids employ specimens immersed in a liquid medium, the ultrasonic beam impinging from the liquid on to the solid, after traversing which it is either (1) reflected from a steel plate to return to the source so that the whole system forms an interferometer with compound medium (MASON [9]), or (2) transmitted to a hydrophone so that the attenuation with and without the sample in the medium can be determined.

The first method is more suited to the kilocycle range. The theory is simple. If c_0 is the known velocity in the liquid, c in the solid of thickness t, d the displacement of the liquid interferometer peaks by interposing the solid: $- c/c_0 = l/(l \pm d)$; the plus sign being taken when the solid possesses a lower velocity, the negative when it has a higher velocity than that of the liquid.

MASON measured the specific impedance of a number of types of rubber in this way.

The theory of the second method has been developed by REISSNER [10]. If longitudinal waves and normal incidence alone are concerned, the ratio of the intensity transmitted through the solid to that of the liquid which it displaces is:

$$\frac{4N^2}{(M^2 - N^2 - 1)^2 + 4M^2}$$

Where

$$M = \frac{\varrho}{\varrho_0 c_0}\left[\frac{u}{\tan\varphi} + \frac{c}{\tan\psi}\right]$$

and

$$N = \frac{\varrho}{\varrho_0 c_0}\left[\frac{u}{\sin\varphi} + \frac{c}{\sin\psi}\right]$$

c is the usual longitudinal velocity; u that of dilitational waves in the solid, φ and ψ are determined by the resonant conditions in the plate, *i.e.* $\omega l/u$ and $\omega l/c$ respectively.

When the shear velocity can be neglected (as in most metals) the ratio becomes

$$1 + \frac{1}{4}\left[\frac{\varrho_0 c_0}{\varrho c} - \frac{\varrho c}{\varrho_0 c_0}\right]\sin^2\frac{\omega l}{c}\,.$$

MASON applied this principle to rubbers at megacycle frequencies. Earlier BÄR and WALTI [11] had used it for glasses.

If the angle of incidence is not zero, the expressions for M and N involve both it and the refracted angle for each wave. It is then indeed possible, as MASON points out, for N and the transmission to be zero owing to the phases of the two waves at the second face opposing each other. Though, in practice, this annulment will never be exact, for the two waves will have different rates of transmission — neglected in REISSNER's theory — in the plate.

Other methods for solids employ the material in air. In order to investigate the propagation of ultrasonics in extended solids, it is necessary to pass on the vibrations to a rod. This rod may be directly stuck to one face of the quartz (*vide supra*) or the crystal may transmit its oscillations to the rod through oil in a sealed vessel. The latter is the method adopted by RÖHRICH [8], who has investigated half-metre rods of steel and copper of various thicknesses at frequencies between 50 and 400 kc/sec. If the axis of the rod is perpendicular to the crystal face, longitudinal vibrations are excited in it; if the axis is parallel to the face, transverse vibrations may be excited.

GIEBE and SCHEIBE [12] discovered that when such a rod vibrates in a space from which most of the air has been withdrawn, a glow discharge is set up in each vibrating segment, while LUDLOFF [13] passed a light beam through the "transparent" material and examined the interference bands in the transmitted light set up by the pattern of nodes and antinodes.

MASON and McSKIMIN [14] measured the velocity of ultrasonic pulses along rods, wide compared to the wave-length and several feet long, using both longitudinal and shear generators stuck on one end by beeswax. The pulses are reflected end to end of the rod, and the echo intensities follow an exponential law of decay, which is compared with that produced by an electrical signal attenuator, adjusted until the electrical and ultrasonic attenuations match.

Hiedemann [15] and his collaborators at Cologne have adapted their optical diffraction methods (see Chap. V) to the study of transparent solids. Thus Hoesch and he were able to photograph the diffraction fringes in the beam of light cast athwart a glass rod caused by the ultrasonics with which it was irradiated. It is not possible to get such great accuracy as in liquids with this method, because irregularities of temperature cannot be avoided. There is also the difficulty, which Schaefer and Bergmann [16] noticed, of getting pure compressional waves into a solid in contact with a piezo-electric source. Even if the ratio of frequency to diameter of rod is such that radial waves are avoided, there may be set up flexural (shear) waves and torsional waves whose optical effect can to a certain extent be sorted out by polarising and subsequently analysing the incident light. It arises from the theory of the stress-optical effect that the double refraction of a light beam in inhomogeneously strained media is a maximum where the direction of maximum strain makes an angle of 45° with the plane of polarisation. Using this fact Hoesch has been able to distinguish the velocity of transverse waves from that of longitudinal waves in a glass rod and so find Poisson's ratio for the specimen.

Bär and Walti [11] have also used the optical diffraction technique, but they immerse the specimen in a liquid, making the diffraction test on the latter medium. The material — which need not be optically transparent — is in the form of a narrow slip cut to a wedge. The quartz generator is applied to one side of this at a height above the tip which determines the thickness of the wedge to be traversed. In the liquid which bathes the specimen, one makes an optical examination looking for failure of transmission from the quartz at levels for which the thickness is a multiple half wave-length. If the ultrasonic beam is incident obliquely it is possible to set up transverse as well as longitudinal waves (*vide supra*). The longitudinal component can be totally internally reflected at a suitable angle of incidence, leaving only the effect of the transverse mode to be detected in the liquid outside.

An interesting extension of this method to measure velocities of sound in solids has however been reported. Bez-Bardili [17] employs the opaque screen, pierced by a number of holes in front of the light source, in the same fashion as Bär, and gets the spots drawn out into diffraction lines after passage of the light through the cell which contains xylol. If a transparent solid in the form of a prism is placed

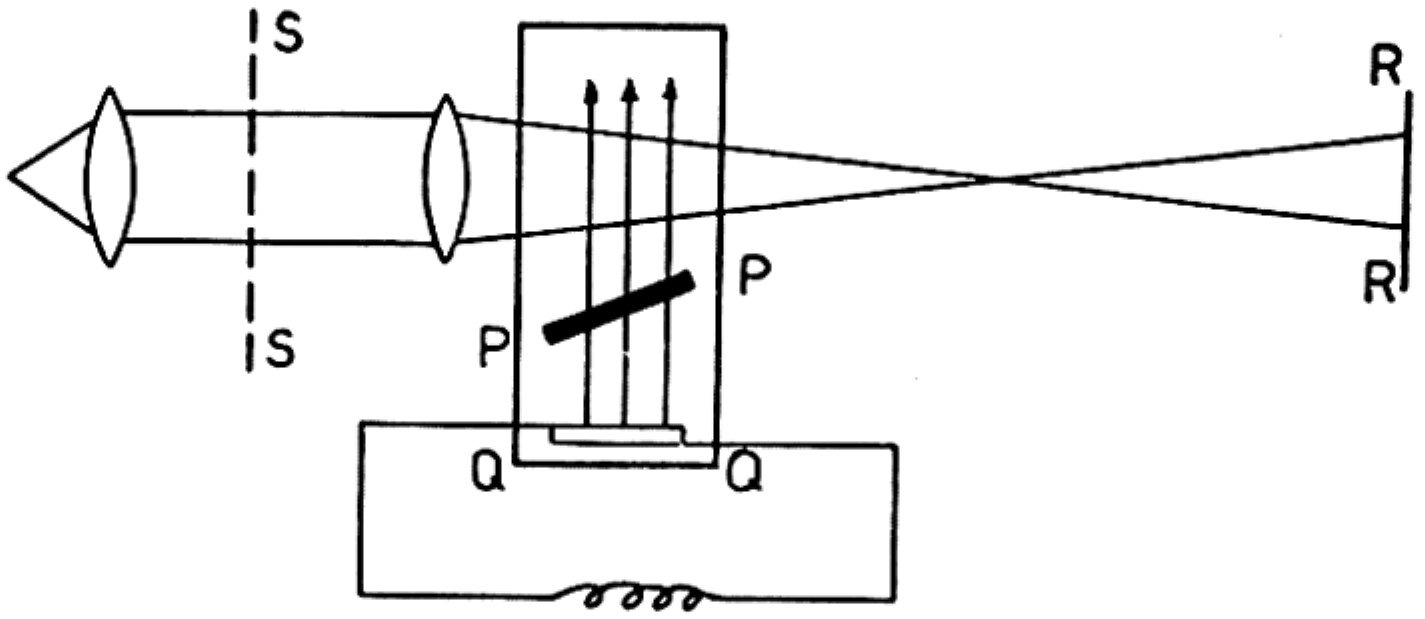

Fig. 86. Velocity in Plate by Optical Diffraction Method (Bez-Bardili)

in the cell, the refraction of the sound waves through it may be observed by the relative lengthening of the spots at different points in the field, and hence the velocity of sound in the solid calculated. In an alternative device (Fig. 86) a plate PP of the material is placed in the cell interrupting the ultrasonic radiation from the quartz QQ. The diffraction of the light spots in the disc SS falling on the screen RR show that some ultrasonic radiation is reflected and some transmitted, but on turning the plate about a vertical axis total internal reflection ensues and the transmitted wave disappears. This angle, is, of course, the critical angle from xylol to the solid. The velocity in the liquid having already been found, that in the solid is obtained. The apparatus, therefore, works on the same principle as the familiar Wollaston apparatus for light waves.

LINDSAY [18] and his school at Providence have studied the resonance in rods and metal crystals using both the powder method and a Rochelle salt pick-up which can be moved along the vibrating solid to detect the positions of nodes and loops without seriously loading the rod. HUGHES, PONDROM and MIMS [19] use a pulse method.

BAKANOWSKI and LINDSAY [20] have used this pick-up to measure the velocity in crystalline rods, both agglomerates of aluminium crystals and single crystals of aluminium (18 cm long and 1 cm in diameter approximately). The dispersion of the velocity with frequency in this crystal is shown on Fig. 87. The other curves round about 300 kc/sec are of a type which SCHOENECK [21] ascribes to torsional —

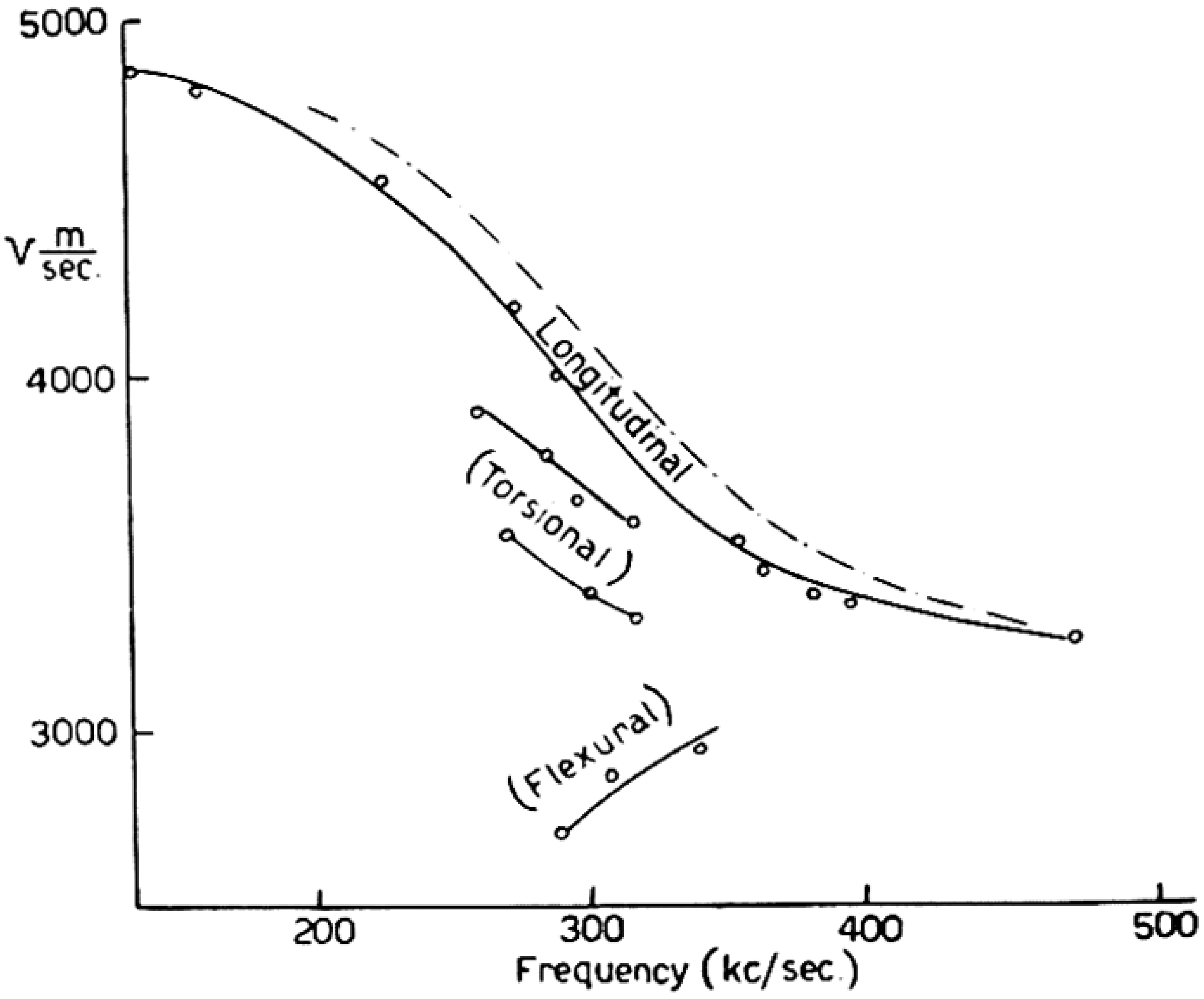

Fig. 87. Transmission in Crystalline Rods as Function of Frequency (Bakanowski and Lindsay)

falling velocity — and flexural — rising velocity — modes The dispersion is, as in a fluid column, due to coupling between radial and axial vibrations.

Scattering by agglomerates of crystals in rods is described in Chap. VIII.

Smyth and Lindsay[18] point out that when such a medium is stratified into layers of different density, it may act as a filter, becoming selective to certain frequencies.

Bhagavantam[22] and his colleagues, using a modification of the optical method of Bär and Walti, measured the elastic constants of diamond, calcite, sodium nitrate and other crystals which have three different velocities of transmission of compressional waves, parallel to the three principal axes. As source they use a quartz or tourmaline wedge which in a tuned oscillator circuit acts as a generator of ultrasonics of frequency variable within certain limits. They have found too, that it is possible to transform flexural waves in the solid into longitudinal waves in the liquid bath, where they are detected.

Focke, Lindsay and Wilks [23] placed the rod, made of a single crystal of bismuth about 10 cm long, between two sections of steel, driving the composite system from a loudspeaker and detecting the modes by two piezo-electric pick-ups. Hence the velocity in the crystal at two orientations to its principal axis was measured at frequencies between 6 and 12 kc/sec. These velocities were, of course, not identical.

We have already (p. 26) referred to the peculiar elastic properties of Rochelle salt. The propagation of pulses

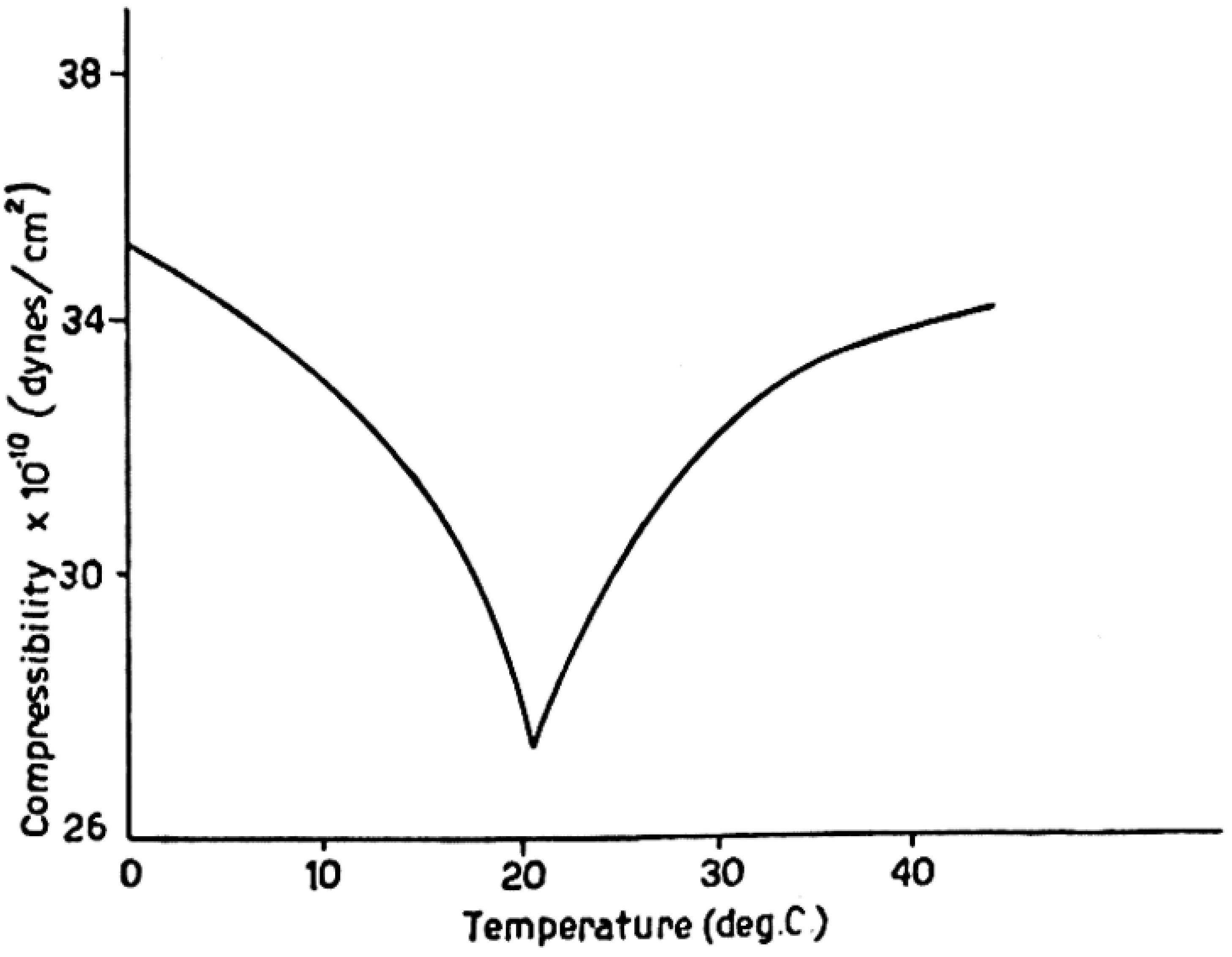

Fig. 88. Compressibility of Rochelle Salt at Various Temperatures (Price)

through this material involves the shear compressibility. Using waves of 10 Mc/sec frequency, PRICE[24] has shown that this factor — measured as ϱV^2 — attains a very low value at the Curie transition temperature (between two crystal forms) of 22 °C, rising on either side (Fig. 88). At this temperature, the attenuation in fact becomes so great that it is wellnigh impossible to measure the velocity of propagation.

Attenuation in Rochelle salt is high probably as a result of the conversion of mechanical energy into electric losses, more so with certain shear constants which are known to involve early departures from Hooke's law near the Curie point. Losses due to electro-mechanical coupling and dielectric losses are however, not easy to sort out from losses inherent in the experimental method such as beam spreading, pulse distortion, and ultrasonic scattering, all of which tend to enhance the true lattice distortion effects. On the latter, the polarisation field has a large effect near the Curie point.

3. Propagation in Rubber-like Materials

Measurements can be made using the pulse technique and a specimen suspended in a liquid medium as NOLLE and MOURY[25] have done, also IVEY, WITTE, MROWAN and GUTH[26]. Their results for velocity in butyl gum are shown in Fig. 89 at various temperatures. All curves show dispersion, which is greater round 0 °C than at 40° higher or

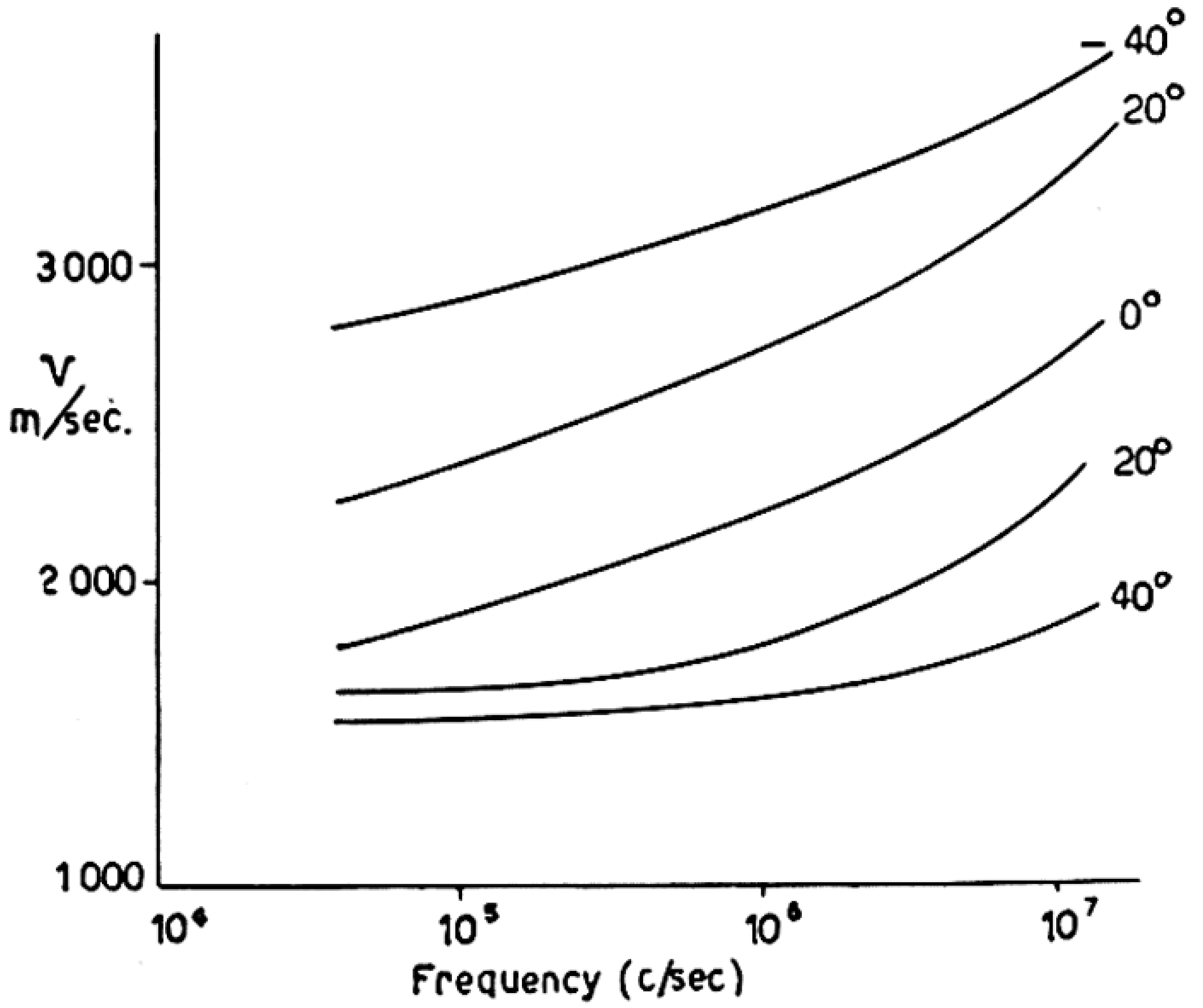

Fig. 89. Velocity in Rubber as Function of Frequency and Temperature (Ivey, Mrowan and Guth)

lower. In natural rubber, the maximum dispersion occurs at —20 °C, but overall it is less than in the synthetic form.

When the attenuation was measured and plotted against

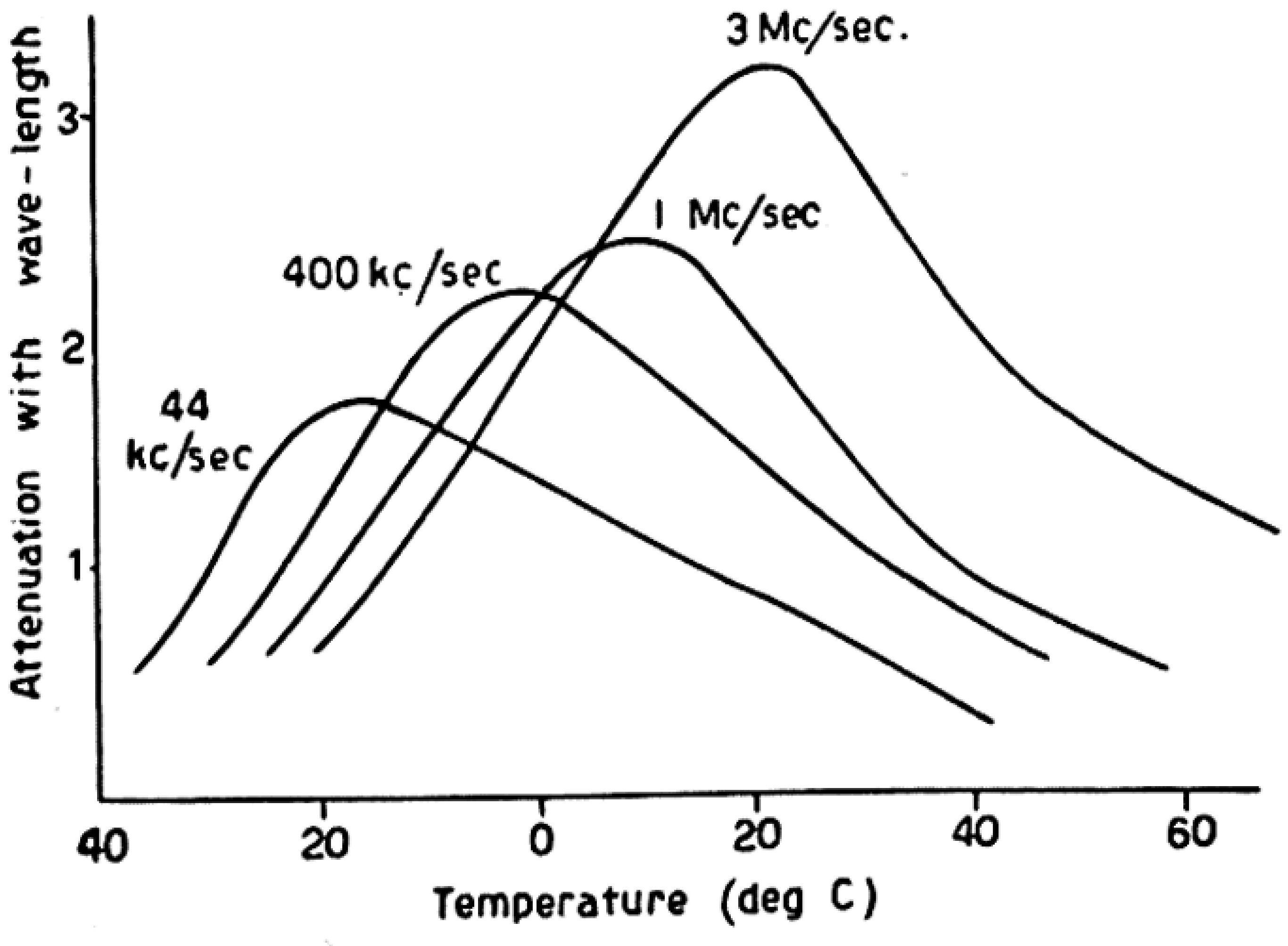

Fig. 90. Attenuation in Rubber as Function of Frequency and Temperature (Ivey, Mrowan and Guth)

temperature, a peak of definite form was found, but the summit-level and its place on the frequency spectrum rose with frequency (up to 3 Mc/sec) Fig. 90. The data agree in general form with those obtained at audio-frequencies, using a stationary wave pattern on strips of rubber. The results indicate a relaxation in the transmission of compressional waves of the type we shall discuss in the next chapter (p. 235), which decrease in value as the temperature rises. Attempts to generalise the kinetic theory of rubber elasticity by analogy with that of ferro-magnetism are now being started at Notre Dame University, where the above work was carried out.

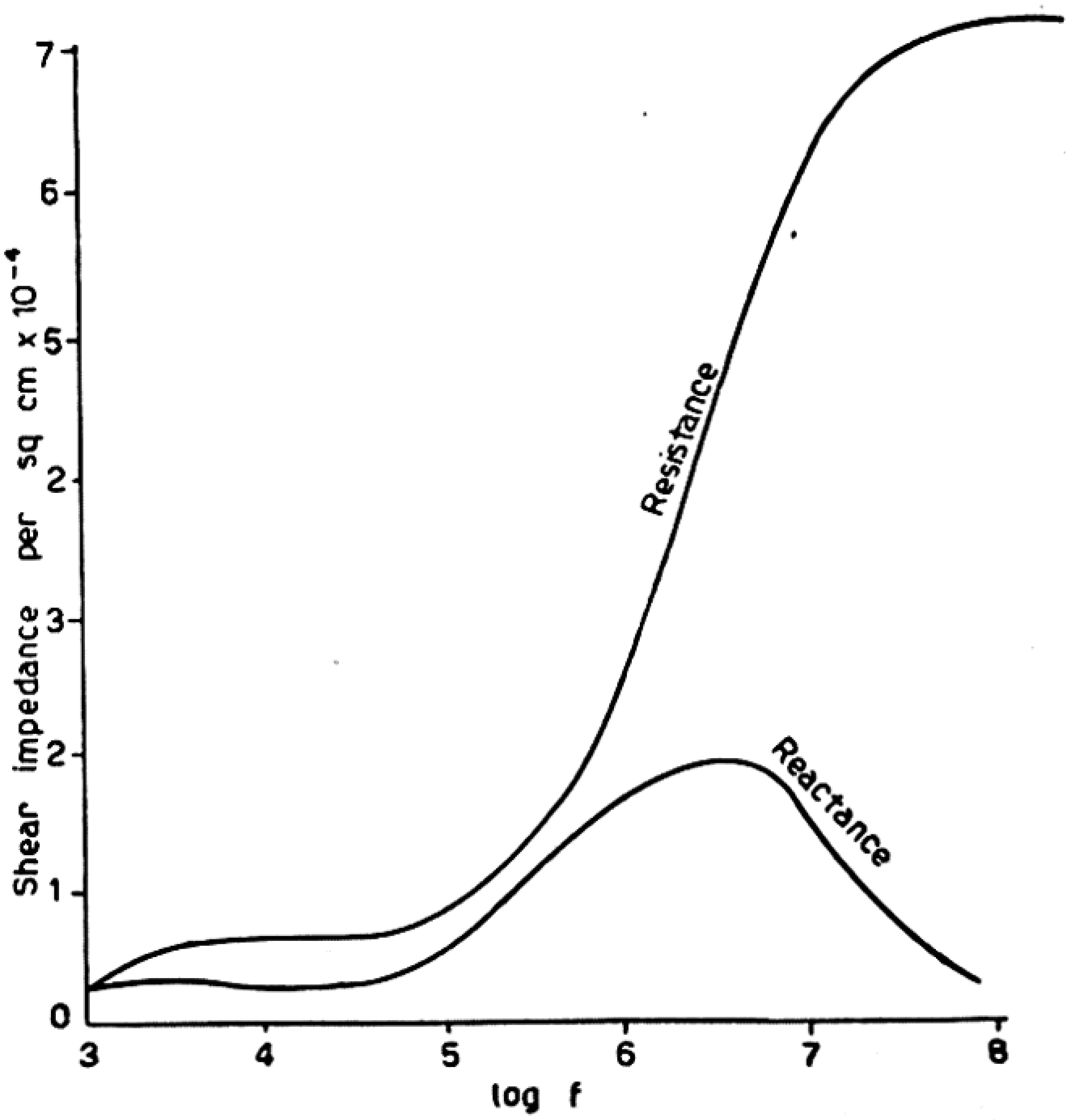

Fig. 91. Shear Impedance in Rubber (MASON)

Fig. 91 (after MASON), showing how the resistance and reactance in rubber and similar substances should vary with frequency, on the assumption of a single frequency of relaxation, should be compared with Fig. 78, p. 196.

4. Propagation in High Polymers and Fibres

In the preceding chapter we referred to elastic effects in high polymer liquids. In the solid state similar effects have been noted, especially in plastics like polyethylene and nylon. WILLARD [27] has adapted the method of BÄR to this end. The specimen is so placed as to interrupt half the ultrasonic beam traversing a liquid. On emergence of this part of the beam its phase is compared optically with the uninterrupted portion at the same level. If, furthermore, the sample is transparent and cut in the form of a wedge, a schlieren analysis of the transmission (p. 43) will show refraction of the sound beam and allow the velocity in the plastic relative to that in the liquid to be calculated.

To measure attenuation, McSKIMIN [28] fixes a slice of the material between fused quartz rods and places a crystal transducer at either end. One of these may emit pulses to be received, after passage through the composite rod, by the other to get the diminution of amplitude by successive reflections. Or each may pulse at one and the same time into the rod while one, connected to the oscillograph, acts as detector of both the transmitted pulse (from the far end) and the reflected pulse (returning on itself). The signal strengths are then adjusted in sending until these two received signals are of equal amplitude. Moreover, the frequency can be varied and the relative phases of the signals adjusted until the two picked up just cancel. So the frequency of the half wave-length and the attenuation in the rod can both be calculated.

In polyethylene, there is definite evidence of dispersion with a relaxation near 10 Mc/sec attributed to shear waves.

Ballon and Silverman [29] have found rather similar effects in the transmission in fibres of high polymers, though they use sonic and the lower ultrasonic frequencies. Work of the same nature has been done by Hillier [30] who sent sonic and ultrasonic waves along filaments of polythene up to 12″ long, picking up the amplitude by a quartz microphone saddled across the filament at different distances.

His results for V (m/sec) and a (cm^{-1}) together with the elasticity modulus E (dynes/cm^2) are shown in the Table below at various temperatures.

Such data can be analysed in terms of viscous relaxation in the manner already noted for elastic liquids.

t	$E \cdot 10^8$	1 kc/sec		2 kc/sec		5 kc/sec		10 kc/sec		16 kc/sec	
		V	a	V	a	V	a	V	a	V	a
0°C	26.0	1041	0.005	1066	0.010	1108	0.019	—	—	—	—
10°C	10.92	866	0.005	903	0.013	926	0.032	944	0.047	0.960	0.086
30°C	5.30	608	0.008	615	0.017	639	0.035	650	0.077	670!	0.114
40°C	4.60	510	0.007	520	0.022	35	0.068	538	0.105	547	0.138

5. Ultrasonic Lenses

A useful application of suitably shaped solid pieces immersed in liquids is to form lenses for concentrating the radiation, as first suggested by HOPWOOD [31] and realised by BEZ-BARDILI [32]. More recently ERNST [33] and SETTE [34] have studied the conditions for the efficient use of ultrasonic lenses. The latter figures a contact lens of plexiglas, which is particularly suited to direct application to quartz, as it has a specific impedance intermediate between that of this solid and most liquids. The combination (Fig. 92) is thus a less expensive alternative to the concave quartz generator of GRÜTZMACHER (p. 9). In the figure the quartz QQ is backed by a metallised hollow cell A containing air, while GG is the plano-convex lens of plexiglass.

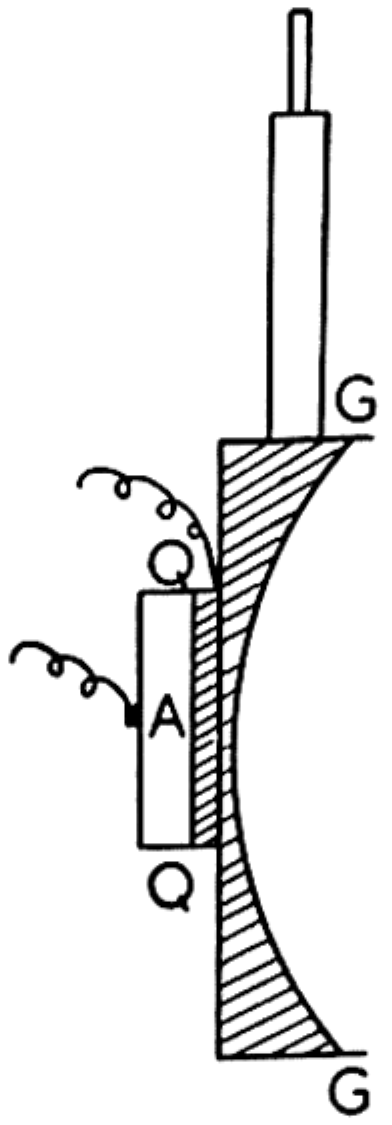

Fig. 92. Ultrasonic Lens (SETTE)

When a substance can be fashioned into a lens, a measurement of the focal length d at high frequency, though not susceptible to great accuracy, gives the refractive index of the solid in the liquid, for this is equal to $(1 - r/d)^{-1}$ for a plano-convex lens, r being the radius of the curved side.

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VELOCITY IN RODS AND WIRES

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CHAPTER VII

THEORIES OF ANOMALOUS PROPAGATION

1. Relaxation Theory

We have in Chapter V animadverted on the concept of a relaxation time in the behaviour under vibration of a liquid known for its elastic properties. Similar ideas have been put forward in explanation of the behaviour of polyatomic gases, such as carbon dioxide at high frequencies where there was no *a priori* reason for anticipation of relaxing of the molecules. Although this was not the historical order in which these ideas were founded, we shall follow TISZA[6] and SCHALLAMACH[7] in first trying to explain these phenomena purely on grounds of anomalous viscosity.

The idea that molecules at sufficiently high frequencies might relax was put forward by JEANS[1] and — for a dissociating gas — by EINSTEIN[2], though at the time the problem was thought to be purely an academic one. After ultrasonic dispersion of velocity in carbon dioxide was discovered, HERZFELD and RICE[3] suggested that the effects could be explained in terms of a relaxation time of order 10^{-5} sec.

In this theory it is supposed that the energy passed on through a system of molecules begins as translational, so that each one gets a pull or push in the direction of propagation of the waves, but that the molecules begin to convert this external energy of translation into internal vibrations (or rotations), like a train of railway wagons impelled by a locomotive, before passing it on. At high frequencies, the compressions follow each other more rapidly than these "relaxations" can take place: but when they succeed each other more slowly the molecules can convert the energy into internal energy. Consequently, at sufficiently high frequencies the speed with which the sound wave passes through the system increases. The form of the variation of velocity with frequency envisaged by this theory — two level lines connected by a short upcast at the critical frequency — is exactly like that predicted by DEBYE's relaxation theory for dielectric constants at high frequency. At the same time, this relaxation upsets the phase relationship between particle-velocity and pressure in the sound wave, and this in turn is apparent as an enhanced absorption of the sound.

In more scientific terms, GROSSMANN [4] states the theory thus:

"In a fluid which contains not only translational (external) energy but also rotational or vibrational (internal) energy, the number of molecules excited in rotation or vibration is a function of the temperature. In most cases a finite time is necessary to establish equilibrium between temperature and internal energy, and one which is peculiar to each rotational or vibrational degree of freedom. One can thus suppose that every molecular state, *i.e.*, every quantum of rotation or vibration, takes a certain time to set up ("relaxation time"). If for a particular quantum state this time is so large that it can only partially or not at all follow the adiabatic temperature changes in the sound wave, so that when the temperature rises or falls no more energy can be taken or given up, then the specific heat becomes less as the frequency rises by an amount representing the energy quantum involved. The velocity of sound is accordingly raised.

The absorption of sound is also affected. Since the energy of translation does not at once take up its equilibrium value, the pressure which is proportional to this energy experiences a phase displacement relative to the oscillating density, and acoustic energy is turned irreversibly into heat."

The rise in the dispersion curve of a gas occurs then, according to this theory, when the time-period of the sound approaches the mean relaxation time of the molecules. In this way HERZFELD and RICE predicted a value of 10^{-5} sec for the relaxation time in CO_2. The same authors obtained an expression for the rise in velocity to be expected. This has been put in several forms by different authors [5]. The treatment which follows is due to HENRY.

Let Q be the actual energy and Q_T the energy which the molecules would have at equilibrium at temperature T, and suppose that

$$\frac{dQ}{dT} = \frac{1}{\tau}(Q_T - Q_0) \tag{44}$$

where τ is the period of relaxation of the vibrational energy. If the gas is subject to adiabatic variations of temperature

$$T = T_0 + T_1 e^{\iota\omega t}$$

then

$$Q_T = Q_0 + C_\omega T_1 e^{\iota\omega t} \tag{45}$$

C_ω being the specific heat of vibrations. Substituting in (44) and solving, we find

$$Q = Q_0 + C_\omega T_1 (1 + \iota\omega\tau)^{-1} \cdot e^{\iota\omega t}\,. \tag{46}$$

If the total specific heat C' be regarded as made up of two parts, C_ω due to vibrations and C_1 due to translation (+ rotation)

$$C' = C_1 + C_\omega (1 + \iota\omega\tau)^{-1} \tag{47}$$

where C' is complex: also, as usual $\gamma' = 1 + R/C'$, R being the gas constant, and the velocity of plane waves is $\sqrt{\gamma' p/\varrho}$.

Hence

$$\gamma' = 1 + R\,[C_1 + C_\omega/(1 + \iota\omega\tau)]^{-1} \tag{48}$$

and is also complex.

The real part of the term in square brackets is

$$\frac{C_\omega + C_1 + \omega^2\tau^2 C_1}{(C_\omega + C_1)^2 + \omega^2\tau^2 C_1{}^2}\,. \tag{49}$$

$C_1 + C_\omega$ is the total specific heat when $\omega \to 0$. Thus the usual specific heat at constant volume in the expression for the velocity of sound is replaced by the reciprocal of (42).

When ω approaches the value $(1 + C_\omega/C_1)\,\tau^{-1}$ a rise in the square of the velocity occurs from the normal $V_0^{\,2} = [1 + R/(C_\omega + C_1)] \cdot p/\varrho$ to an ultimate value $V_\infty^{\,2} = (1 + R/C_1) \cdot p/\varrho$.

The relaxation time τ is also linked with the probability that a given molecule will be excited in vibration or rotation. The smaller this time becomes the greater will be the number of excited molecules at any instant. On this theory, the effect of impurities on relaxation time is to increase the number of excited molecules of the (originally) pure gas, and so increase the probability that a molecule will be in the excited state. Collisions with dipole molecules or molecules with which the original ones have a chemical affinity should be most effective in this sense.

The theory of HERZFELD and RICE implies a relaxation of the compressibility. Now STOKES wrote for the coefficient of viscosity $\frac{4}{3}\eta + \varkappa$, of which the first term is the usual viscous effect (p. 106) and the second a correction to it which STOKES neglected in a first approximation.

Let us now write the propagation constant k in this form:

$$k = \omega \,/\, \sqrt{\varkappa/\varrho} - \iota a_1 \tag{50}$$

where a_1 is the (frequency-dependent) part of the total absorption a. If a_1' stands for $a - a_1$

$$V^2 \left(1 + \frac{\iota V a_1'}{\omega}\right)^{-2} = \frac{\varkappa}{\varrho} = \frac{C_p}{C'} \cdot \frac{1}{\varepsilon}$$

where ε is the isothermal compressibility.

Writing further $\Delta = C_p - C_v$, and using (40) for C':

$$V^2 = \frac{1}{\varepsilon\varrho}\left(1 + \Delta\,\frac{C' + C_1\omega^2\tau^2}{C'^2 + C_1{}^2\omega^2\tau^2}\right) \tag{51}$$

$$\alpha' = \frac{1}{2\varepsilon\varrho}\cdot\frac{\omega^2}{V^2}\,\Delta\,\frac{C_\omega\tau}{C'^2 + C_1{}^2\omega^2\tau^2} \tag{52}$$

which are similar in form to the formulae of dispersion and absorption already obtained.

Kneser[5] points out that the velocity V at any frequency f can be expressed in terms of V_0, V_∞ and the frequency f_m at which the maximum absorption a_m occurs thus:

$$V^2 - V_0{}^2 = (V_\infty{}^2 - V_0{}^2)\,(f/f_m{}^2)\,[1 + (f/f_m)^2]^{-2} \tag{53}$$

and the absorption per wave-length μ as

$$\frac{\mu}{f^2} = \frac{2}{V}\cdot\frac{a_m}{f_m}\cdot\frac{1}{1 + (f/f_m)^2}\;. \tag{54}$$

In terms of viscous relaxation, (52) gives

$$\mu = \pi\Delta\,\frac{C_\omega\omega\tau}{C'(C' + \Delta) + C_1(C_1 + \Delta)\omega^2\tau^2} \tag{55}$$

(53) and (55) are identical with (51) and (52) if the specific heats are expressed in terms of the velocities and τ in terms of f_m.

On the other hand, we might argue that the fluid possesses an acoustical reactance in the Maxwellian sense and a complex viscosity (*cf.* p. 196)

$$\eta' = \frac{\eta_0\,(1 - i\omega\tau)}{1 + \omega^2\tau^2}$$

which we can introduce into the proceeding equation to get

$$\frac{V}{V_0} = 1 + \frac{2}{3}\left(\frac{\eta_0\omega}{\varkappa}\right)^2 \left[\frac{\varkappa\tau}{\eta_0} \cdot \frac{1}{1+\omega^2\tau^2} + \frac{1-\omega^2\tau^2}{(1+\omega^2\tau^2)^2}\right] \quad (56)$$

η_0/τ being the "rigidity" at very high frequencies. On this view, there could be both viscous and elastic dispersion in a fluid.

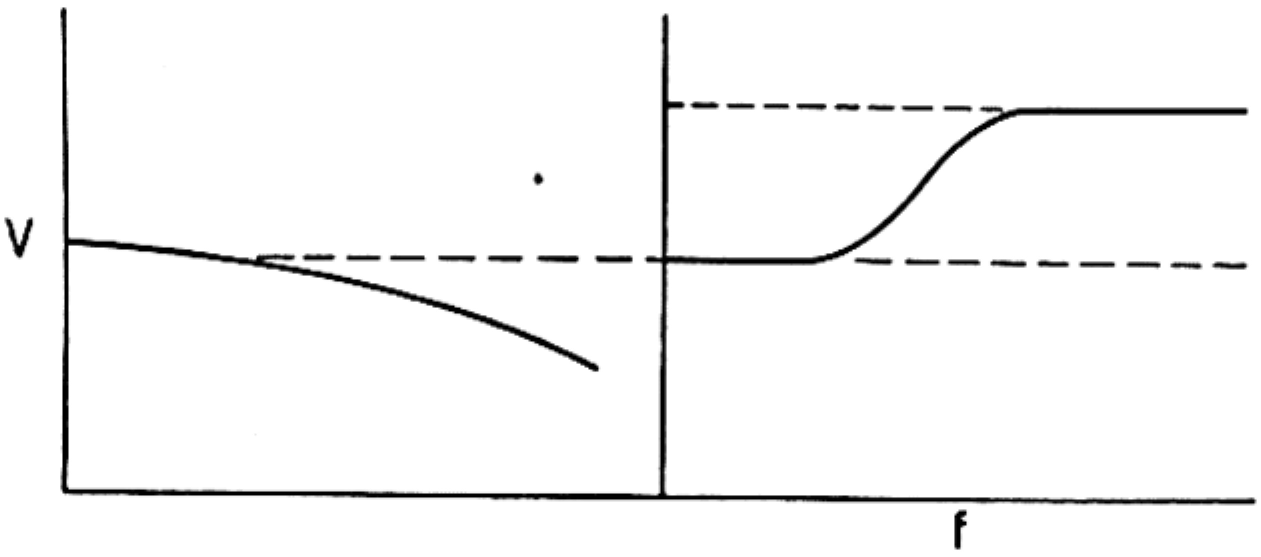

Fig. 93. Theoretical Types of Velocity Dispersion

Fig. 93 indicates two possible types of dispersion. That on the left is a simple "negative" dispersion in which the velocity falls steadily as the frequency rises. That on the right is the type envisaged by the simple relaxation theory. Neither exactly copies the experimental curve in carbon dioxide, (*cf.* Fig. 46), but a combination of these two hypothetical dispersions would well model the actual trend of velocity in carbon dioxide.

2. Application of Theory to Gases

We have already noted in Figs. 39—41 of Chapter IV the observed dispersion, which agrees well with these ideas except for a tendency of the velocity to fall both before and after the "step up".

The absorption, too, in such gases is much greater than the Kirchhoff value, but, in spite of this, there is no marked heating of the gas, such as one observes in liquids when they strongly absorb.

In gaseous mixtures showing dispersion it is supposed that in an unexplained way the molecules of the adulterant act as catalysts to the main gas, if present in the right proportions, affecting the rate of transfer from one type of energy into another.

It should be noted that the hypothesis here outlined is a purely *a posteriori* one. The mean time of relaxation of a molecule on this hypothesis can be calculated if the frequency at which the change-over from low-frequency velocity to high-frequency velocity is measured experimentally, but there is no independent experimental approach to the problem as yet — and in only one case has the relaxation time been calculated *a priori*. The problem of calculating the time of relaxation for simple molecules considered as harmonic oscillators is to find the number of collisions necessary, on the average, to produce an augmentation of the vibrational or rotational energies at the expense of the translational. As this augmentation can only take place by discontinuous jumps, and requires more energy of translation than the molecules may possess individually, each collision is not effective: but one can calculate the percentage of molecules having the requisite velocity, bearing in mind the type of collision — end on, broadside, *etc.* — required to produce a vibration or rotation as the case may be. VAN PAEMEL and MARIENS[8] have thus predicted for the latter transformation mean times of $2 \cdot 10^{-4}$ sec for oxygen and $1.3 \cdot 10^{-9}$ and $6.6 \cdot 10^{-10}$ sec for hydrogen and deuterium respectively at N.T.P. Although one experimental result corroborates the former value, most workers have failed to record any dispersion of the velocity of sound in oxygen, while the other two frequencies lie too high at present for certain experimental confirmation.

The possibility of influencing the molecules to react specifically to high-frequency sound by the addition of catalysts has already been mentioned. Other experimenters have tried to "excite" the molecule by physical means.

DWYER[9] has described experiments in which the after-effect of collisions produced when a discharge passes through a gas is evidenced by the persistence of absorption lines in the visible spectrum for a short time after the discharge has ceased. While these experiments give credence to the "relaxation theory" in its original form, they have no necessary connexion with ultrasonic dispersion, since DWYER made no ultrasonic experiments on the gas in question (iodine).

The author[10] has attacked the same problem from a different angle. Attempts have been made to find a direct effect on the well-known ultrasonic dispersion of carbon dioxide by subjecting it to optical radiation of its own natural (vibrational) frequencies. A Pierce acoustic interferometer was constructed of the usual type, save that the centre portion, including the region between the quartz oscillator and the reflector, was provided with quartz windows. The apparatus was evacuated and filled with carbon dioxide. Frequencies between 90 and 100 kc/sec for the ultrasonic source were used, corresponding roughly to the peak of the dispersion region for the gas in question. The infra-red radiation came from a hot tube containing carbon dioxide of the original RUBENS and ASCHKINASS type, and was focused by mirrors on to one of the quartz windows.

Two experiments were tried. In the first, the beam emerging from the opposite window was passed through a Hilger infra-red spectrometer and the intensity of the 4μ, 8μ and 15μ lines of carbon dioxide compared when the quartz was quiet and when it was set in oscillation, to see if the ultrasonic energy caused any change in the absorption of these radiations. No positive effect was found, though this was not surprising in view of the limited amount of ultrasonic energy which one can get into a gas at such frequencies, and the already small residual infra-red energy after the gas had exercised its selective absorption.

In the second experiment, the gas was again irradiated at the three infra-red wave-lengths quoted, and measurements made of the wave-length and dissipation of the ultrasonic energy in the gas. No change in wave-length, other than that which could be attributed to the rise of temperature, was found, but the ultrasonic attenuation was definitely greater when the gas was irradiated than when it was not, as though the molecules, excited in their natural vibrational states, were able to absorb more of such energy.

It, is however, difficult to generalize from this result in respect to the relaxation theory, since a mere increase in thermal agitation of the molecules, induced by rise of temperature and irrespective of any particular natural mode of vibration, produces a change in the ultrasonic dispersion.

FRY [11] is experimenting with the action of infra-red rays on an ultrasonic interferometer containing carbon dioxide, with a different object in view as he hopes to use this induced change of ultrasonic absorption as a detector of infra-red, but the experiments are not sufficiently far advanced for detailed report. KRYDRYAVTSEV, however, finds that *air* irradiated with ultraviolet light has a somewhat less ultrasonic absorption than ordinary air.

VAN ITTERBEEK and THYS [12] have found no increased absorption of ultrasonics in oxygen in a magnetic field. Neither they nor any other workers have been able to influence or produce relaxation by means outside the domain of acoustics.

3. Scattering and Diffusion Theories

The suggestion that cases of high attenuation, without undue heating, were due to the radiation being scattered out of a forthright beam was first made by LUCAS for liquids and was demonstrated in carbon dioxide in the dispersion region by the author [13], subsequently confirmed by MOKHTAR and SHEHATA.

Firstly, if the reflector experiments are repeated, using an artificially roughened reflector so as to scatter the radiation that falls on it, a marked smoothing of the antinodal peaks occurs in oxygen as the distance of the reflector from the source is increased. On the other hand, little change is produced in carbon dioxide and nitrous oxide when the scattering reflector is substituted for the plane one. From this one concludes that in the latter gas scattering by the gas itself is already taking place and is increased but a little by the superposed artificial scattering of the reflector. Secondly, traversing of the hot wire from side to side of the tube, at a distance sufficiently great to avoid the region close to the quartz face, showed a spreading of the radiation in carbon dioxide, much greater than in oxygen or argon. From these two experiments we conclude that the observed dimunition in amplitude in carbon dioxide is due to dispersion in the complete sense, *i.e.*, to both scattering and absorption of energy on the part of the molecules. This leads one to another aspect of the behaviour of these anomalous gases, *viz.* that the molecules of the gases in which these effects are most marked are all notably anisotropic. They are, in fact, just those which in view of their limited degrees of freedom, show the Raman effect and allied light scattering phenomena most readily. Both effects are, for example, strong in carbon dioxide and nitrous oxide, less in sulphur dioxide and oxygen, negligible in argon.

As to the possibility of a change in wave-length during scattering, this, if it existed, would be difficult to sort out from true absorption. Thus, if an original pure sine wave after dispersion consists of a group of waves covering a small interval of frequency, we should need to take our equation (49) and allow ω in the second term to vary within narrow limits, so that the resulting measured velocity would be that of a group. The net effect of true absorption and interference of this type on either stationary or progressive waves will be rather similar to that of absorption alone. Each will produce, in progressive waves, a steady diminution of amplitude, and in stationary waves, a smoothing of the peaks. With the accuracy at present available, the hot-wire apparatus could not disentangle the two effects.

The similarity between Fig. 26 and 46 suggests anomalous dispersion as an alternative to relaxation (or in addition) as an explanation of the observed facts, but one could scarcely postulate resonators of the type made for BELIKOV's experiment [14] as existing in a gas like carbon dioxide. It is more likely that an "ordered disorder" may be set up in the gas, which has the same effect on the sound waves, at the dispersion frequency, as that which turbulence in the atmosphere has on the propagation of sound.

4. Application to Liquids

Following KNESER [15], BAUER [16] and others see in the abnormal absorption of liquids the beginnings of a dispersion region whose peak lies beyond the experimental range of frequency. Thus Bauer gives the following table for the

Substance	Excess of $\alpha/f^2 \cdot 10^{17}$ expt.	V_0 m/sec expt.	V_∞ m/sec calc.	$2a_m$ calc.	f_m Mc/sec calc.
Carbon disulphide	10,800	1140	1250	0.644	52.5
Benzene	830	1310	1530	1.300	1200
Carbon tetrachloride	513	910	1090	1.593	3420
Chloroform	380	987	1100	0.835	2230
Toluene	84	1310	1440	0.823	7500
Acetone	60	1170	1270	0.614	8720
Ethyl bromide	56	932	1070	1.137	21800

predicted dispersion in liquids, based on equations (53), (54) and (55).

Unfortunately for the theory, no dispersion of the velocity has been confirmed. Only one of these liquids, carbon disulphide, has a calculated relaxation frequency within the limit of acoustical experiment, yet shows no rise of velocity.

Of the others, toluene and acetone have had their hypersonic (BRILLOUIN) velocities compared with the ultrasonic values without showing evidence of dispersion (*cf.* Chap. V).

HALL [17] points out that any quasi-crystalline model of a liquid, in which a molecule is supposed to lie in a potential well for a time τ before jumping into a neighbouring well when in an excited state, leads to a relaxation of part of the compressibility. There will be a static and a dynamic compressibility depending on whether the motions have periods short or long compared to τ.

Hall writes for the pressure amplitude

$$p = \varkappa_\infty + \frac{\varkappa_0 - \varkappa_\infty}{1 + i\omega\tau} \tag{57}$$

$$\frac{a}{f^2} = \frac{2\pi^2}{V}\left(1 - \frac{\varkappa_0}{\varkappa_\infty}\right)\frac{\tau}{1 + \omega^2\tau^2} \tag{58}$$

The quantity $\varkappa_\infty$, arising from uniform decrease in the intermolecular distance — aside from re-arrangement — such as occurs in crystals, may be estimated from the known compressibility in the solid state.

By taking trial values for $\varkappa_\infty$, Hall is able to show that his theory faithfully follows the observed change of absorption with temperature in water.

Another possibility exists in solutions in which a chemical reaction may take place at a rate which is a function of pressure. Sound waves may influence this reaction to an extent dependent on amplitude and frequency. Lieberman [18] has introduced this idea to explain the abnormal absorption at frequencies in the neighbourhood of 1000 kc/sec. (The theory is formally similar to that applied by Einstein to the propagation of sound in a partially dissociated gas like nitrogen tetroxide). In seawater magnesium sulphate is believed to be the molecule which undergoes ionic dissociation and introduces a partial compressibility.

To sum up the relaxation theory as it applies to liquids: Dispersion may arise from several causes.

(1) The viscous term in k (eqn. 50) introduces a small positive dispersion at high frequencies. (This has, however nothing to do with relaxation).

(2) Either of the viscosities in eqn. 50 may be complex if the molecule has certain equilibrium positions or potential wells between which it oscillates at a finite frequency (τ^{-1}). A complex shear viscosity has so far only been established in visco-elastic liquids (p. 192).

At very high frequencies the velocity approaches the "solid value":

$$\sqrt{\left(\varkappa + \frac{4}{3}\eta\right)/\varrho}$$

noted in connection with glycerine (p. 197).

(3) The bulk modulus may become complex because of a time lag in the equilibration between external and internal degrees of freedom.

As we have seen, although the mechanisms of (2) and (3) are different they lead to similar results. Even if one grants that relaxation in inelastic fluids has been established, it would seem wellnigh impossible to disentangle the basic causes.

5. Absorption in Solids

Landau and Rumer [19] have tackled the theory of ultrasonic absorption in solids, following a line of reasoning somewhat similar to that of Lucas[20]. The absorption is supposed to arise from interaction between ultrasonic quanta and Debye heat quanta, of which the wave-lengths must be large compared with those of the sound: this implies low temperature. The ideas are developed as follows. A plane sound wave represented by the vector l and pulsatance ω collides with a wave of thermal agitation: l_1 and ω_1. Within classical bounds no interchange of energy can take place between them, otherwise the principle of superposition could not hold. But if cubic terms are included in the expression for the energy density — which implies distortion — then transitions take place by which energy and momentum are carried over from the sound wave into the Debye wave, so that the outcome is a new wave (l_2 and ω_2). Then $l_2 = l + l_1$ and $\omega_2 = \omega + \omega_1$, but as with most of these quanta exchanges, $\lambda_2 < (\lambda + \lambda_1)$. Hence the thermal waves in the solid must have a smaller velocity than that of the sound for this process to take place, and so absorption due to this cause is most likely to occur as between *transverse* sound waves and *longitudinal* thermal waves.

6. Propagation in Liquid He II

Landau[21] considers that He II behaves as though it were a mixture of two liquids, which are in different quantum states. By reason of this fact there can exist simultaneously currents of the same liquid flowing in opposite directions, but only one exercises a force on a body placed in its path.

The second form has zero entropy and viscosity, and probably all He II would be like this at 0 °K.

He supposes then that this substance consists of a mixture of normal and superfluid constituents in which the total momentum is zero

$$\varrho u_n + \varrho_s u_s = 0$$

and the kinetic energy is derived from the entropy flow (S') in a reversible change:

$$\frac{1}{2}\left[\varrho_n u_n^2 + \varrho_S u_S^2\right] .$$

The rate of change of kinetic energy per unit volume is then

$$\varrho \varrho_n u_n \left[\frac{1}{\varrho_{S'}} \cdot \frac{\partial u_n}{\partial t}\right] ,\ \text{neglecting}\ \partial \varrho_S / \partial t .$$

If the volume changes by δx we multiply by this and equate to the flow of entropy, *viz.*: $-\varrho S u_n S T$.

So:

$$S\,\frac{\partial T}{\partial x} = -\frac{\varrho_n}{\varrho_S} \cdot \frac{\partial u_n}{\partial t} = \frac{ST}{C}$$

S being the entropy at temperature T, and C the specific heat.

But:

$$\frac{\partial T}{T} = \frac{\partial S}{C}$$

So:

$$\frac{\partial u_n}{\partial T} = -\frac{\varrho_S}{\varrho_n} \cdot \frac{ST}{C} \cdot \frac{\partial S}{\partial x} .$$

Also in the entropy flow

$$\frac{\partial}{\partial x}(\varrho S' u_n) = -\frac{\partial}{\partial t}(S'\varrho) .$$

If we treat S and ϱ as constants with respect to position, we get from the last two equations

$$\frac{\partial^2 S}{\partial t^2} = \left[\frac{\varrho_S}{\varrho_n} \cdot \frac{S^2 T}{C}\right] \cdot \frac{\partial^2 S}{\partial x^2} \,. \qquad (57)$$

The quantity in brackets is the velocity of the thermal waves in this substance as derived by Landau, though the treatment here follows Gogate and Pathak [22].

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CHAPTER VIII

ULTRASONICS IN DISPERSE SYSTEMS

1. Propagation in Aerosols

The absorption of ultrasonics in aerosols (smokes, mists, *etc.*) and in hydrosols, (powders in liquid suspension, emulsions *etc.*) has formed a bye subject of investigation for those who are primarily interested in pure gases and liquids. The attenuation of an ultrasonic beam arises in the main from the scattering produced by the objects in suspension, particularly when their size is comparable with the wave-length of the radiation, and is also a feature in solids having a granular structure.

Besides this, in fluids there are forces accompanying the radiation which tend to break-up, disperse or coagulate the discrete particles, which we must also discuss.

SEWELL [1] obtained an expression for the absorption of sound waves in a medium in which solid (rigid) spheres were in suspension in a fluid, under the conditions that their diameter is small compared to the wave-length and that the factor $\sqrt{\omega/\nu} \cdot d/2$ is large; also, the volume occupied by the spheres must be small compared to that of the container.

His expression is:

$$\alpha = \frac{N\pi d^2}{4}\left[\frac{12\nu}{cd} + \frac{3\sqrt{2\omega\nu}}{c} + \frac{7}{144}\cdot\frac{\omega^4 d^4}{c^4}\right] = $$
$$= \alpha_1 + \alpha_2 + \alpha_3\,. \qquad (58)$$

N = number of particles per ml.
d = diameter of particles.
ν = the dynamical viscosity.
c = velocity of sound.
ω = pulsatance.

The first two terms in the brackets of the equation (α_1 and α_2) are frictional terms and represent the incident energy lost by friction. The last term (α_3) gives the loss by scattering. Actually the most important term is the first, and as an approximation the absorption can be written in the form $\alpha = 3N\pi d/c$. For most smokes at ultrasonic frequencies the orders of the three components are: α_1, 10^{-2}; α_2, 10^{-4}; α_3, 10^{-8}.

SEWELL assumed the particles to be immobile spheres, but when a particle is very small and the wave-length large, it will tend to move with the oscillations (*cf.* p. 33) and decrease the effective frictional terms; in an appendix to his paper he made a correction for such mobility.

BRANDT, FREUND and HIEDEMANN[2] have also examined the conditions under which this mobility of the particles takes place. Their results indicate an increase in the absorption, at the frequency increases, for small particles. LAMB[3] has adapted STOKES' expression to flexible spheres, *i.e.* to mists and emulsions but, in fact, such distortion is a small effect except in the case of gas bubbles in liquids at some resonant value of the imposed frequency.

Most of the systems in suspension encountered are polydisperse, that is to say, they are composed of particles of various sizes of which the size-distribution function must be determined if the resulting attenuation is to have any meaning to those who follow the research. When solid powders are suspended, the function may be determined by letting the specimen settle under gravity in a suitable and still liquid and applying Stokes' law to relate free-falling velocity in the liquid to diameter of particle. Samples of liquid drops in mists or emulsions are usually analysed by collecting them by impact on to a microscope slide and counting and measuring them under a microscope.

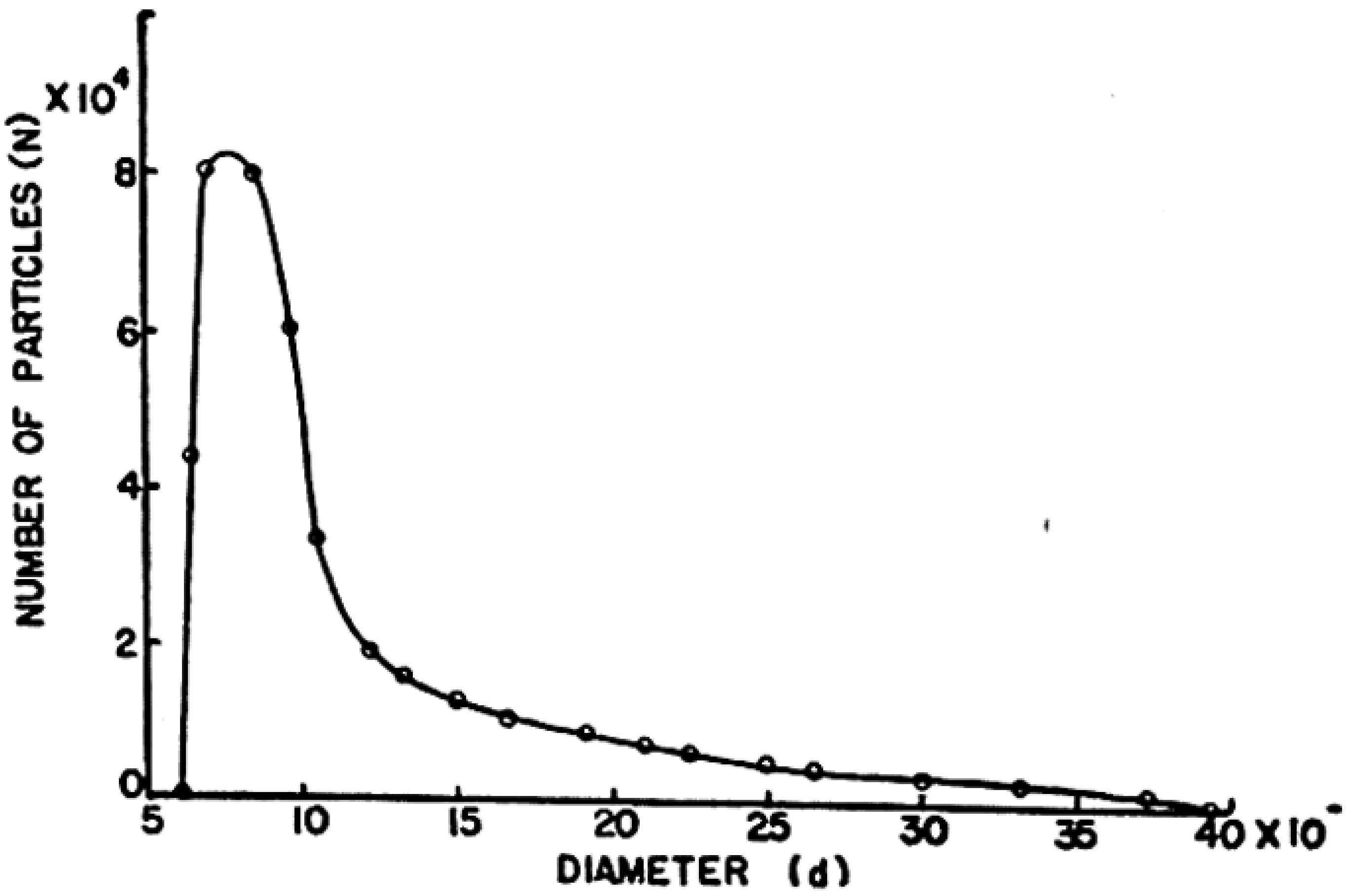

Fig. 94. Particle-size Distribution in Suspensions (LAIDLER and (RICHARDSON)

LAIDLER and the author [4] have done this using smokes made of stearic acid or magnesium oxide, the absorption being measured in a variable-path interferometer.

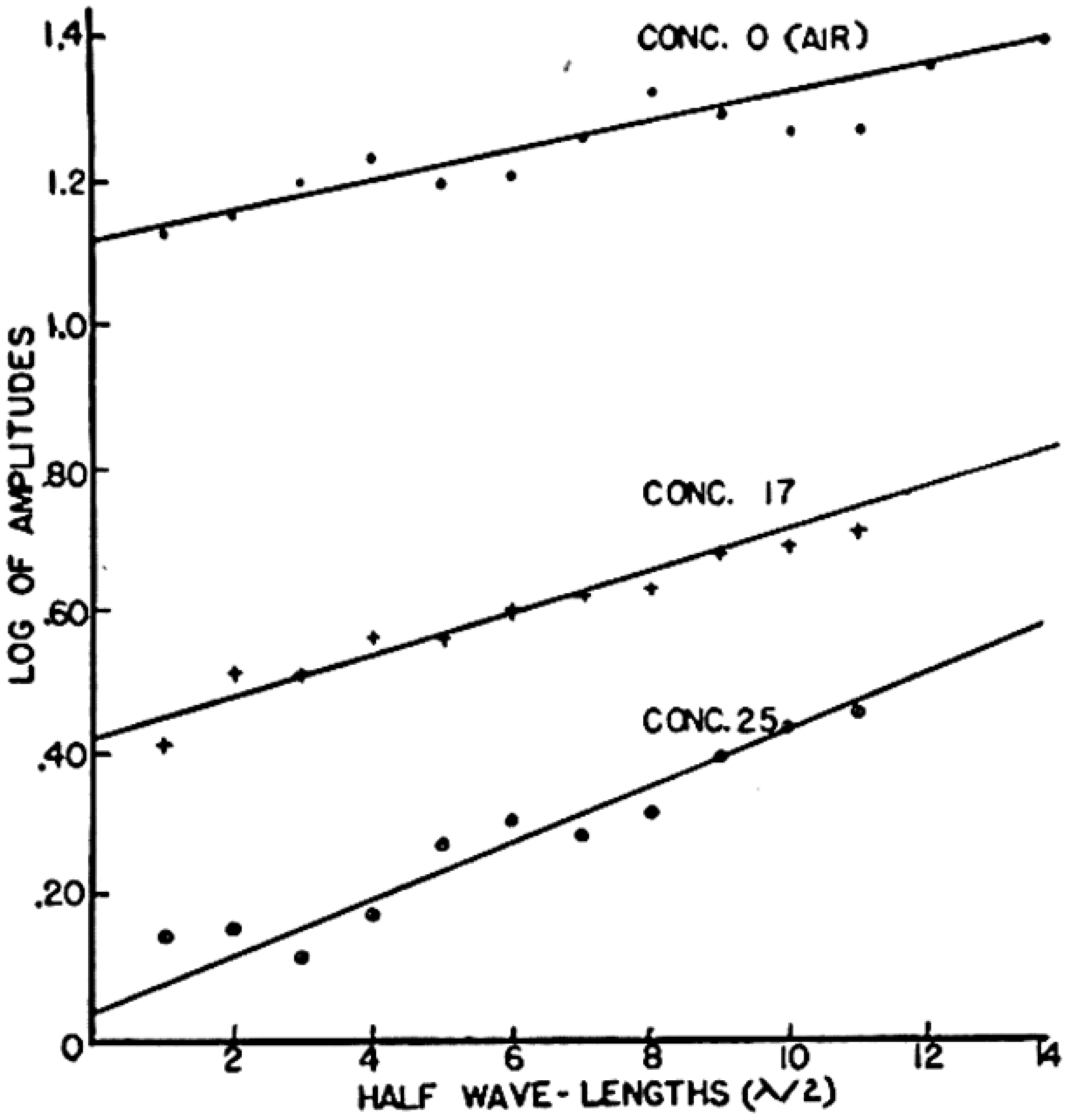

Fig. 95. Attenuation of Ultrasonics in Suspensions (LAIDLER and (RICHARDSON)

Fig. 94 is an analysis of a typical stearic acid (candle) smoke, having a maximum (by number) at 8 microns diameter. The interferometer results for this smoke at two concentrations, also for air, are shown on Fig. 95, for a frequency of 42 kc/sec. From the slope of the lines (after correction for beam spreading, p. 51) the absorption coefficients for the smoke can be calculated.

For comparison with equation (58) it is better to employ a mono-disperse system. It was found that the spores of certain fungi were suitable for this purpose. Those of *lycoperdon* for instance are all close to 4 microns in diameter and spherical.

The density of the spores was found by floating them in a suitable alcohol-water mixture: hence N, with a knowledge of the total mass in suspension and the radius (observed under the microscope).

The values of N, r, ν and c were substituted in STOKES' expression with the three frequencies employed (42, 98 and 695 kc/sec). In the Table below the total calculated absorptions are compared with experimental values.

Frequency kc/sec	42	98	695
$\alpha \cdot 10^2$ cm^{-1} (theory)	3.71	4.07	5.77
$\alpha \cdot 10^2$ cm^{-1} (expt.)	2.9	3.1	3.9

The absorption due to the change in frequency of the sound waves is shown by α_2 but this effect is small, and so, by theory, the variation of absorption with frequency should be a small quantity, except when the size of the obstacle approaches the wave-length. In actual practice, it was found that α increased very gradually with the frequency.

This is confirmed by the only other work known on the absorption of sound waves in smoke, which was done by ALTBERG and HOLTZMANN[5] in tobacco smoke. They used a rod, excited in longitudinal vibrations by continuous friction, as source and a pressure vane as detector. The frequency range was from 5 to 20 kc/sec, and the absorption coefficient in a smoke of density $7 \cdot 10^{-5}$ g per ml rose from 0.0025 to 0.014 in this range. As they made no analysis of their smoke, comparison with theory is not possible.

EPSTEIN[6] considers that a correction may be necessary in a fine mist because the particles may have a periphery comparable with the mean free molecular path (10^{-5} cm at atmospheric pressure). KNUDSEN, WRIGHT and ANDERSON[7] have shown that the actual attenuation in a natural fog at low frequencies is of the magnitude predicted by SEWELL's theory — the mean diameter being about 12 microns.

By using an oscillating circuit of small power in our smoke investigation, it was possible to avoid rapid coagulation at the frequencies considered.

To test this point a second sedimentation curve for the stearic acid was taken after it had been irradiated by the ultrasonics for some minutes. The curve with or without previous irradiation is shown on Fig. 94 and shows no notable effect of the ultrasonics on the coagulation. Such change as does exist may be due to one or other of the acoustic causes discussed by the authors just cited, or it may be due to electrical precipitation by the potential field of the electrodes, a cause that they do not appear to have envisaged, but which is a recognised method of precipitation in industrial chemistry.

The sedimentation lasted for about forty minutes, after which time no variation was shown in the readings taken. Inasmuch as considerable natural coagulation must have occurred during this period the distribution curve obtained gives greater weight to the larger particles than was probably the fact at the time of measuring the absorption.

So far we have dealt with suspensions of particles of spherical form. The particles in a number of powders, of which bentonite, graphite and vanadium pentoxide are noted examples, are lenticular or even needle-shaped. When an electrostatic — or in certain cases, a magnetic field — is applied to a suspension of such polar particles, they tend to align themselves along the field, even if the latter is

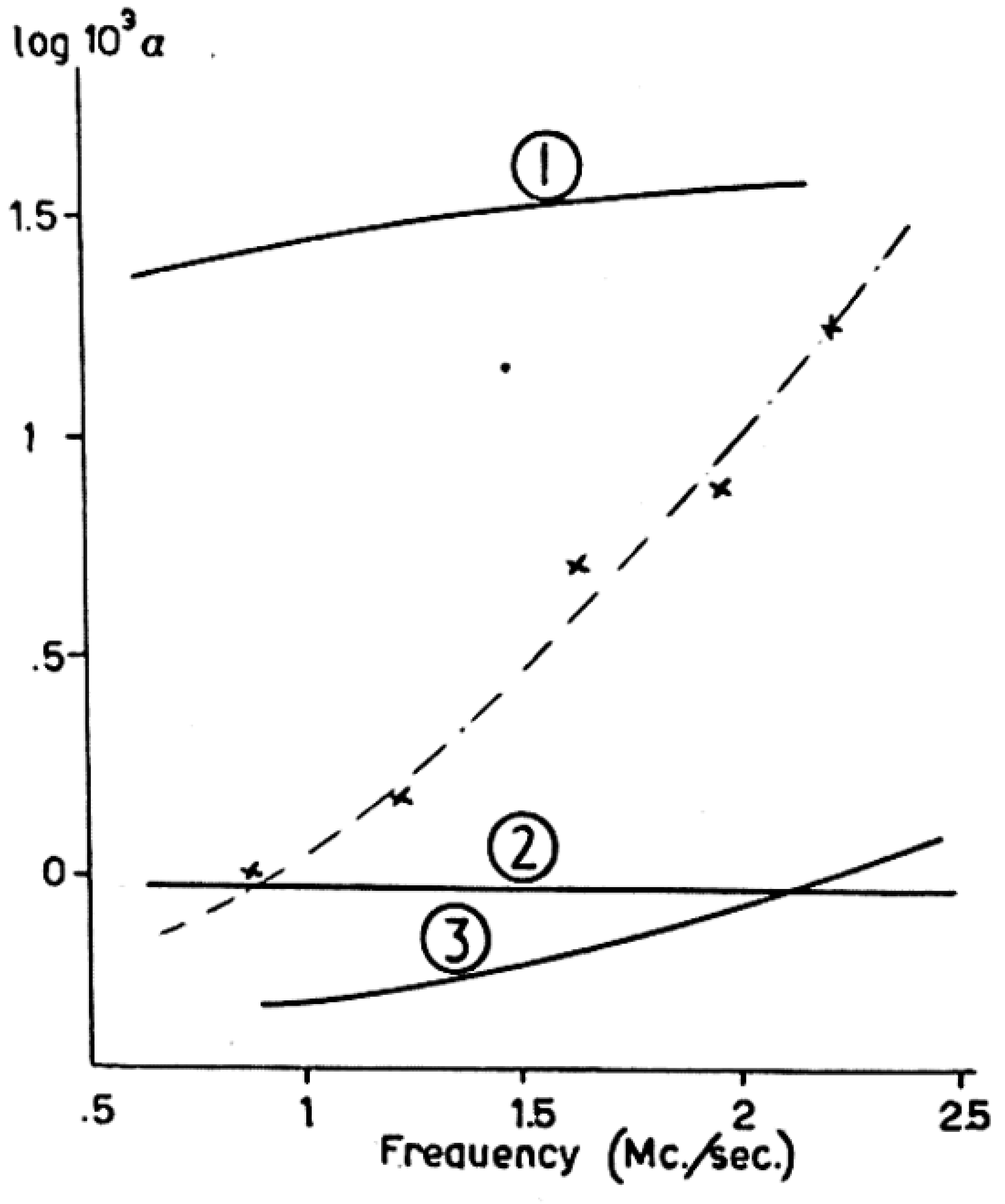

Fig. 96. Contributions to Absorption Coefficient in Suspensions (HARTMAN and FOCKE)

alternating. A somewhat similar effect is produced by an ultrasonic field though the effect vanishes soon after the field is turned off, when the particles gradually resume their random orientation.

Suspensions of *lycopodium* ($d = 50$ microns) in liquids have been attacked by HARTMAN and FOCKE [8] and emulsions of mercury in water by VLADIMIRSKY and GALARIN [9], likewise by GROSSETI [10].

HARTMAN and FOCKE's results are shown in Fig. 96. While they observe the trend of absorption with frequency which SEWELL's theory indicates, the experimental value of α is much more than the sum $\alpha_1 + \alpha_2 + \alpha_3$ of SEWELL's theory.

Frequency Mc/sec	0.97	1.25	1.50	1.74	2.01	2.20	2.46
$\alpha \cdot 10^3$ cm (theory)	0.27	0.42	1.0	1.34	2.0	2.52	3.4
$\alpha \cdot 10^3$ cm (expt.)	3	9	14	15	17	24	34

Their results are shown (connected by a chain line) on Fig. 96, together with the three component theoretical coefficients (augmented one hundredfold). The excess attenuation may be due to multiple scattering not considered in SEWELL's theory. There was also sometimes a tendency to set up stationary waves.

Two phenomena have been observed by previous workers using ultrasonics in smokes, which are not contemplated by the RAYLEIGH-SEWELL theories, *viz.*, the formation of the familiar KUNDT's dust figures and coagulation. Both of these effects have been studied by BRANDT and FREUND [11] and found to be a consequence of the use of high power in the source. PEARSON[12], who used the dust figures to measure the ultrasonic velocity in air, reports that at times the power was sufficient to break the crystal. Investigations have been carried out by BRANDT and HIEDEMANN and by ANDRADE and PARKER [13] to measure the aggregation of suspended particles in gases by sonic and ultrasonic waves. They have found two principal phases of the process. In the first phase, the particles oscillate under the influence of the sound waves, aggregation taking place owing to collision of the particles. In the second phase, the particles are so much larger that they no longer oscillate but describe very irregular motions, as observed by ANDRADE for lower frequencies. During the second phase, coagulation still continues owing to collision between the enlarged particles and the still oscillating smaller particles. Experiments were performed with varying power and the aggregation of the particles was found to increase rapidly with the power employed.

2. Acoustic Birefringence

A sol is often acoustically double-refracting. This effect was first observed by LUCAS [14] in pure castor oil. At about the same time OKA [15] drew attention to experiments made by KAWAMUR[16] in a vanadium pentoxide sol and developed a theory of the latter effects. BÖMMEL and NIKITINE[17] have in addition observed that light traversing a sol in this condition becomes partially polarised. If, on the other hand, the incident light is polarised, and transmitted in a direction parallel to the plane of the sound waves, a set of equidistant fringes of light can be seen in the transmission (through crossed Nicols) which correspond to antinodes in the sound waves. The fact that the needles or discs remain set in spite of the alternating sound field is due to the small value of their relaxation time in respect to the ultrasonic period.

The theory of Lucas has been elaborated by PETERLIN[18], who takes JEFFERY's[19] formula for the force tending to orientate an ellipsoid with its major axis along the direction of fluid motion (U) at a rate

$$\frac{\partial \theta}{\partial t} = - Ub \sin \theta \cos \theta$$

where $b = (p^2 - 1)/(p^2 + 1)$ and p is the ratio of the elliptic axes. The orientation is actually an equilibrium between this force and that of Brownian movement, of which the function Φ determines the number of molecules per ml having orientations round θ in an elementary solid angle. For this PETERLIN obtains

$$\frac{\partial \Phi}{\partial t} = Ub \left[\sin \theta \cos \theta \frac{\partial \Phi}{\partial \theta} + (3 \cos^2 \theta - 1) \Phi \right] - D_0 \Delta \Phi \tag{59}$$

D_0 being the coefficient of rotational diffusion, companion of the Brownian movement. The solution — which satisfies the experiments — is

$$\Phi = \frac{N}{4\pi}\left[1 + \frac{3\dot{\xi}_0 b}{c} \cdot \frac{\omega\tau}{\sqrt{1+\omega^2\tau^2}} \cdot \left(\cos^2\theta - \frac{1}{3}\right) \cdot \sin\left\{\omega\left(t - \frac{x}{c}\right) - \tan^{-1}\omega\tau\right\}\right]. \quad (60)$$

Here N is the number of molecules per ml, $\tau = 1/6D_0$ the time of relaxation, and the ultrasonic wave has particle-velocity amplitude $\dot{\xi}_0$ and pulsatance ω, and is propagated along the x axis with velocity c. This shows how the orientation grows with the ultrasonic frequency and remains proportional to it until $\omega\tau$ approaches 1. At this point, Φ is 70 per cent. of its maximum value.

If the axes of the ellipsoids coincide with the optical axes, it is possible to calculate the change of refractive index which results in the birefringence. It is seen from eqn. (60) that the amplitude of the optical effect will be proportional to $N\dot{\xi}_0/c$, that it will oscillate with the frequency of the ultrasonic wave but will lag behind it by the relaxation angle $\tan^{-1}(\omega\tau)$.

From experiments it is possible to calculate the coefficient of diffusion D_0 a quantity not readily amenable otherwise to measurement.

Although this effect was first noted in colloidal solutions, the equations developed by PETERLIN do not then apply without modification as JEFFERY's formula is only valid for very small Reynolds numbers, but optical birefringance has since been found in viscous oils by LUCAS and by ZVETKOV [20] and his collaborators who have verified the main conclusions of the theory and found τ to be of the order of 10^{-7} sec.

3. Vibrating Bubbles and Drops

MEYER and TAMM [21] have initiated work on a subject which seems to have aroused much interest among research workers in the past few years, *i.e.*, the natural frequency and damping of gas-bubbles formed in liquids. Their bubbles were produced by electrolysis of the liquid in a vessel which also contained a magneto-strictive source (15 to 35 kc/sec), and it was noted that the frequency of this source determined the size of the bubbles liberated in such a way that the product of this frequency and the mean diameter of the bubbles was a constant. This is what one would expect if the vibrations of the bubbles were radial. It was also possible to see under the microscope when resonant vibrations of the bubble took place because it then took on a matt instead of a sharply-defined appearance. To obtain the actual resonance curves with a view to calculating the damping coefficient the bubble was allowed to grow in size and then, while still irradiated with the source at the original resonance frequency, the reaction due to the oscillation of the bubble upon a nearby microphone in the liquid was observed. This gave a response: natural frequency curve for the bubble, on the assumption that the natural frequency of the growing bubble at any instant is inversely as its radius. So the damping coefficient in the neighbourhood of a resonant peak was calculated, following the usual theory of forced vibrations. δ was proportional to f. Larger bubbles — in resonance to the range of frequency 1.5 to 7 kc/sec — had their amplitude of forced vibration directly measured by casting an image of the oscillating bubble on a photo-electric cell, in which an a.c. proportional to the amplitude in question was set up.

The effect of the viscosity of the liquid on the bubble

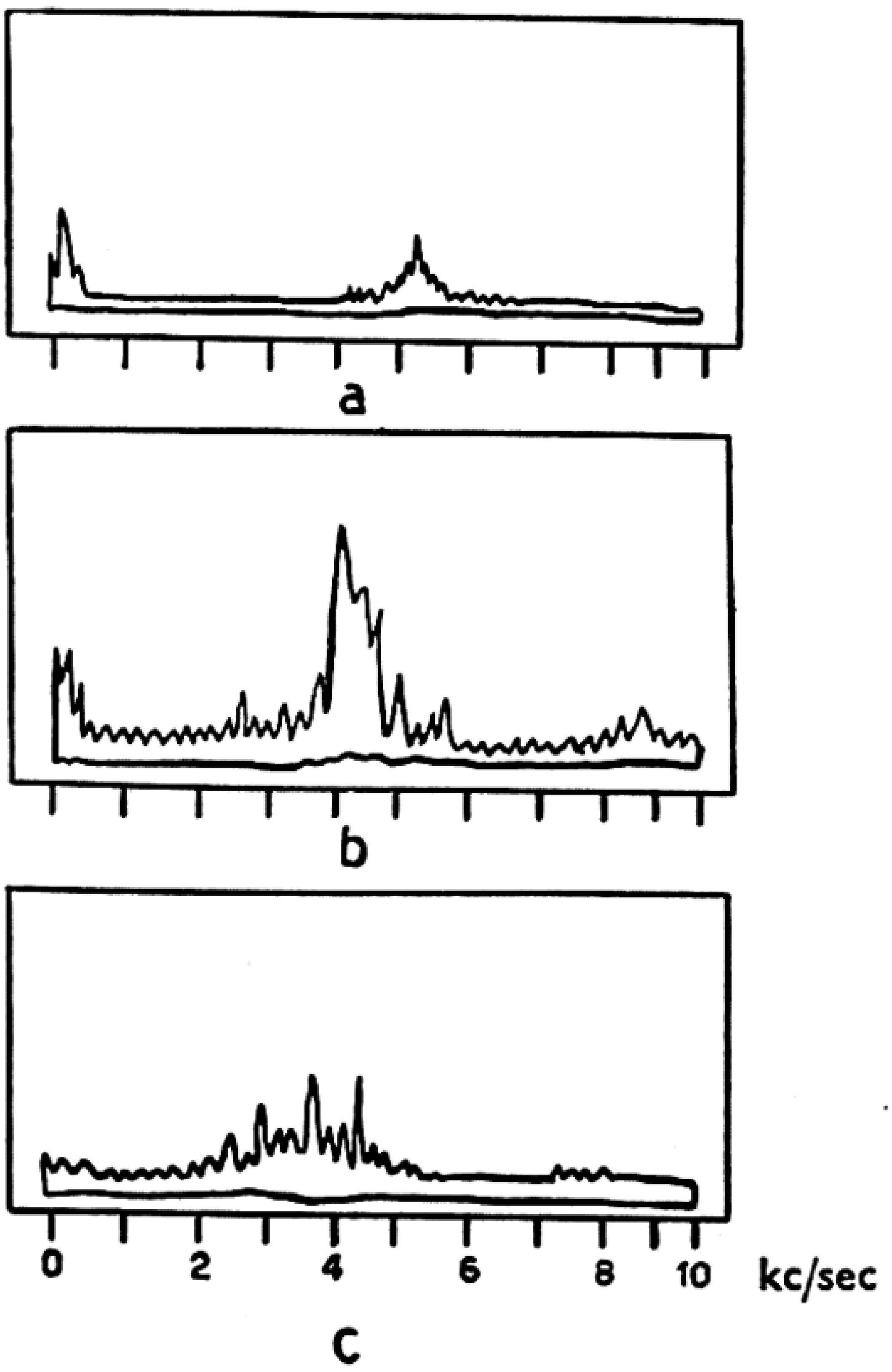

Fig. 97. Resonant Frequencies of Air Bubbles (MEYER and TAMM)

vibrations also came under review. This naturally affected the damping coefficients which also increased in linear fashion with the natural frequency of the bubble. Finally the sound spectrum, in the frequency range up to 10 kc/sec, for the hiss formed by bubbles escaping from a fine jet submerged in water was obtained. Specimens of these are shown in Fig. 97. Their natural frequency shows they have a diameter equal to that of the orifice. Round this value the size : frequency seems to be grouped approximately in the form of a Gaussian error curve.

The frequency of these radial pulsations, in which the bubble changes in size are given by a formula due to F. D. SMITH, *viz.*:

$$\omega^2 r^2 = 3\,\gamma p/\varrho \tag{61}$$

r being the radius of the bubble, p the internal pressure and ϱ the density: γ is the ratio of specific heats. In accord with this MEYER and TAMM found for air bubbles: frequency (in kc/sec) × radius (in cm) = 0.6; some difference between theory and experiment being accounted for by the acoustic loading or "added mass" of the liquid medium. The high values of the damping coefficient — 0.15 in water and 0.7 in glycerine at 4 kc/sec — are to be ascribed to the compressions radiated into the ambient fluid from the pulsating bubble.

WILLIS calculated the work done in this way by the bubble at the expense of the sound energy and so arrived at an approximate value of the attenuation suffered by the sound waves in their passage. A "blanket" of bubbles is in fact a good device for absorbing high-frequency sound waves when they traverse a liquid.

A closer examination of the vibrating bubble, such as KORNFELD and SUVOROV [22] have made, shows the possibility of another type in which the surface of the bubble is divided up by nodal lines of longitude into spherical sectors and the bubble changes shape but not size. The natural vibrations of such a sphere are characterised by an integer m such that, according to RAYLEIGH,

$$\omega^2 = \frac{\sigma}{\varrho r^2} (m + 1) (m - 1) (m + 2) \tag{62}$$

(σ is the surface tension). These vibrations are, on the whole, of much lower frequency than the radial type and are less damped, because they set a much smaller quantity of the surrounding fluid into vibration.

The velocity of sound c in a "bubbly mixture" has been calculated by CARTSENSEN and FOLDY [23] while DAVIES and THURSTON [24] have deduced the characteristic impedance on the assumption that the bubbles are set in vibration at the frequency of the source, r_0 being the "resonant" radius.

If c_0 is the velocity of sound in the medium in the absence of bubbles they find

$$\frac{c^2 - c_0^2}{c^2} = \frac{3\lambda^2}{4\pi r_0^2} \int_0^\infty \frac{r_0^2}{r^2} \cdot G(r) \cdot dr \,, \tag{63}$$

the function $G(r) \cdot dr$ representing the distribution in number of the particles with radius r, supposed greater than r_0.

Beside the damping of energy by the vibrating bubbles which WILLIS discussed, there will be scattering of the oncoming radiation. The scattering function

$$F(r) = \frac{r}{(\omega_0^2/\omega^2) - 1 + i\delta} \qquad (64)$$

δ being the damping coefficient already discussed as a function of frequency (see also below p. 271). The attenuation of sound in a blanket of bubbles to which CARSTENSEN and FOLDY apply these considerations is a combined effect of damping and scattering. They were thus able to calculate the impedance of such a screen and compare the attenuation with that suffered by a plane wave of 20 kc/sec. The size distribution was determined from the rate of rise of the bubbles in water.

4. Dispersion and Coagulation of Particulate Matter

When we study the action of ultrasonics on individual particles we encounter conflicting reports, some workers using the action to break up particles and others to make a particle collide with its neighbours. This is evidently a question of control, especially of the density of population, since a highly-concentrated dispersion tends to coalesce of itself. Starting with coarse bodies, the first action of the ultrasonics is disruptive, but as the numbers increase under this action, a coagulating effect may supervene. Eventually a maximum fineness of dispersion is reached as a balance between these two effects.

MATHIEU-SICARD and LEVAVASSEUR [25] have studied the dispersing action on a barium sulphate hydrosol formed by precipitation, at a mean size of 1 micron. The best dispersion was obtained after about 3 minutes irradiation. The fineness of the dispersion was studied in terms of the light scattered by the suspension, to which it is proportional. A specific effect of the frequency was noted, the best frequency increasing as the initial mean particle size was less.

When two particles are moving in an acoustic or hydrodynamic field there arise forces of attraction (if their motions are in phase) or of repulsion (if out of phase) — the so called "Bjerknes forces" or "actions at a distance".

If the particles are fluid drops or bubbles capable of radial vibration in resonance to the acoustic source (*vide supra*) such radial vibration gives rise to further hydrodynamic forces.

A drop or bubble smaller than the resonant size will tend to vibrate in phase with the exciting force — because the natural frequency is higher — and large ones out of phase with the exciting force. In any case there will be mutual motions of different-sized particles which will encourage coalescence.

The general law of coalescence of those small particles which combine as soon as they collide is

$$\frac{dN}{dt} = H\left(\frac{1}{N} - \frac{1}{N_0}\right). \qquad (65)$$

Where N_0 is the number of particles at the start, N after time t and H is a constant of value about 10^{-9} cm^3/sec in a still medium but much more in a fluid having turbulent flow or irradiated by ultrasonics (H will of course be greater in viscous fluids). Values of H for such cases have not yet been determined but measurements are in hand of the rate of coagulation under controlled conditions of turbulence, either in direct flow or in otherwise still fluid irradiated by ultrasonics.

The workers at the Cologne Institute for Electrolyte Research (BRANDT, FREUND and HIEDEMANN [2]) published detailed results on this subject in which the rate of coagulation is determined not only by a series of micro-photographs at short time intervals, but also by a nephelometric method. This consists in allowing a beam of light to pass through the vessel containing the aerosol and to fall on a photoelectric cell. The extinction of the light is a function of the number N and average radius r of the particles, so that as they diminish in number faster than they gain in diameter by coalescing, the rate of coagulation is indicated by the rise in the photoelectric current. Both these authors and ANDRADE [13] have given theories of the effect based on KÖNIG's work on the behaviour of particles in a sound field of frequency f, (p. 33) but, whereas BRANDT and HIEDEMANN attribute the action to coalescence of particles of different sizes owing to their different mobilities (proportional to $r^2 f$ in their formula), ANDRADE first derives an expression for the attraction of neighbouring particles on the assumption that they remain stationary in the oscillating gas, and then introduces a correcting term for the mobility of the smaller and lighter particles. For the immobile particles he obtains the expression

$$N_0^{\frac{1}{3}} - N^{\frac{1}{3}} = =\chi t \tag{66}$$

where N_0 is the initial number of particles and N that after a time t, χ being a constant independent of frequency (since mobility has been neglected).

5. Grain Refining and Ultrasonic Scattering in Melts

When a liquid, solution or melt, is cooling and tending to crystallise, the size of the embryo crystals or crystallites can be influenced by ultrasonic agitation to have both a smaller and more uniform size range.

In solids, the most spectacular of these applications lies in the refining of the small grains into which aluminium

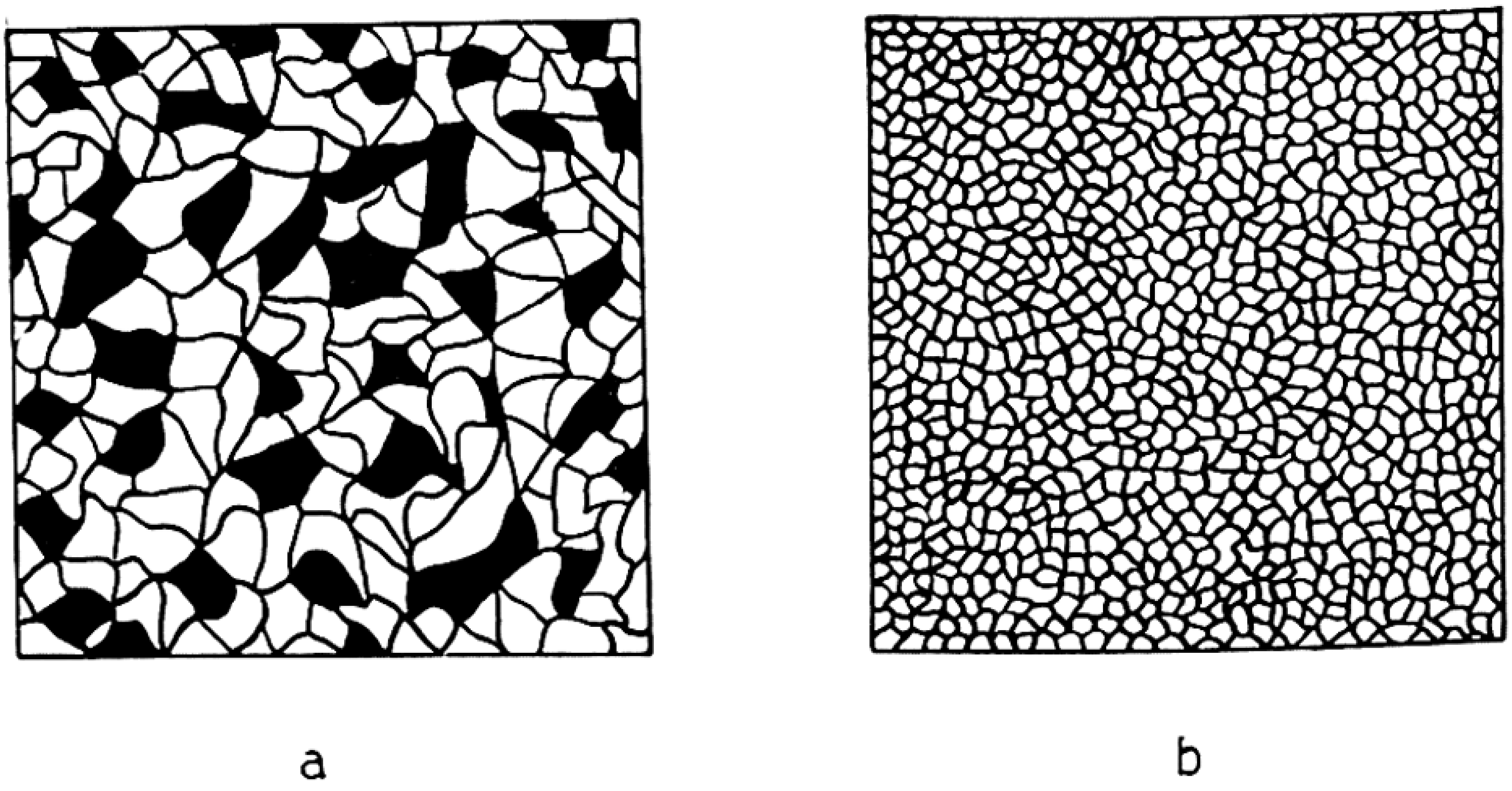

Fig. 98. Aluminium Melts Crystallising (a) without, (b) with Ultrasonic Irradiation (TURNER)

or magnesium crystallises on solidifying from the molten state. Fig. 98 shows drawings of two micro-photographs of the crystallising of aluminium melts, that on the left showing the irregular sizes of crystals resulting from normal cooling, that on the right when the melt is irradiated with ultrasonics during cooling, showing the small and remarkably regular crystals which then result.

It has been observed by MASON and MCSKIMIN [26] that solids having a granular crystalline structure dispersed in an amorphous melt, such as aluminium and magnesium when allowed to solidify in moulds, can scatter an ultrasonic beam of radiation passed through them. The scattered energy is proportional to the fourth power of the frequency and to the volume of the grains, provided the latter have small dimensions compared to the wave-length of the radiation, as in the corresponding optical case. This is true whether shear or compressional waves are concerned, and results in a loss of directly transmitted energy. Using the pulse method, they have, in fact, found two components in this "loss", one proportional to f^4 and another proportional to f. The former is the true scattering by obstacles small compared to the wave-length (*cf.* p. 62), the latter is the usual hysteresis loss in a metal. Little granular effect was shown by glass even at 10 Mc/sec, this material evidently being effectively amorphous. In the metals the fourth power scattering law holds down to wave-lengths three times the mean grain size. After that there is still energy scattered, but more nearly as the square of the frequency.

Following, **Rayleigh** they derive for the scattered energy, from each grain:

$$\frac{2\pi^2 v}{\lambda^4} \cdot \left(\frac{\delta \bar{\varkappa}}{\varkappa}\right)^2 \qquad (67)$$

Here $(\delta\varkappa/\bar{\varkappa})^2$ represents the mean fractional change of compressibility and is proportional to the mean fluctuation of wave-velocity $(\partial\bar{c}/c)$ or of acoustic refractive index, if the density is regarded as constant. The mean grain size having been observed on sections cut for the microscope, a check on this theory can be obtained.

If for example, a rod of metal is cut and a single pulse of ultrasonics sent along the axis, the echo will show a series of peaks — owing to the ricochet of the pulse from end to end — of magnitude, depending on the absorption, diminishing *exponentially*; if the metal is quite homogeneous, but if it has a regular crystalline character like that pictured, the end echoes will be overlaid by irregular reflections from the crystallites. Such scattering is precisely similar to that which occurs when a beam of light passes through a mist. If the grains are much less in diameter than the wave-length, Rayleigh scattering takes place. If the grains are about the same size as the wave-length, a complicated effect is found (*cf.* p. 62).

Finally, when the grains are quite large, the reflected radiation is proportional to d^2 and independent of λ. Specular reflection then takes place.

Roth [27] also **Bastein**, **Bleton** and **De Kerverseau** [28], have measured the attenuation in aluminium and magnesium rods. The former shows that in the range 10 to 80 Mc/sec a rod with a mean grain size of 2 mm (much greater than the wave-length), shows an attenuation almost independent of frequency, but in another rod with grains one tenth of the first, the attenuation rises rapidly with frequency, because the grain size falls within the range of wave-length. The French investigators used a fixed frequency of 2.5 Mc/sec and found that scattering reaches a maximum whenever the melt has grains or other structures of diameter equal to a multiple of $\lambda/2$. This they ascribe to vibration of the individuals, causing anomalous dispersion (*cf.* Fig. 26, p. 65).

When the medium is heterogeneous so that the velocity of sound therein may vary by δc in one place, we may, following DEBYE and BUECHE [29] express the scattered energy in terms similar to those in which the scattering of light is usually described, *i.e.*

$$\int \frac{\delta c_1}{c} \exp. \left[i\beta\,(s, r)\right] dv_1 \,.$$

Where δv is a volume element scattering sound, $\bar{c}$ the mean velocity to a wave-number β, and s and r are the vectorial aspect and distance of a point to which sound energy is scattered.

The amount picked up by another volume *element* δv_2 from the first

$$I = \iint \frac{\overline{\delta c_1\, \delta c_2}}{\bar{c}^2} \cdot \exp.\ [i\beta\, (s, r_1 - r_2)]\, dv_1\, dv_2$$

$$= \frac{\overline{\delta c^2}}{\bar{c}^2}\, v \int \zeta \exp.\ [i\beta\, (s, r)]\, dv \tag{68}$$

wherein ζ is a "correlation coefficient" expressing the temporal relationship between the fluctuations and at two places within the regime. It equals 1 when all fluctuations over v are in phase, 0 when they are completely incoherent.

The amount scattered in all directions.

$$I = 4\pi\, \frac{\overline{\delta c^2}}{\bar{c}^2}\, v \int_0^\infty \zeta\, r^2\, \frac{\sin \beta s r}{\beta s r}\, dr\,. \tag{69}$$

In the case of a monotonic source radiating spherically with λ large compared to the distance over which ζ falls to zero, the proportion scattered up to a distance x from the source

$$\frac{I_x}{I_0} \sim \frac{\overline{\delta c^2}}{\bar{c}^2} \cdot \frac{v^2}{\lambda^4 x^2}\,.$$

Otherwise, if either the spectral function of the fluctuation is known ζ may be calculated; or if the trend of ζ with x is known, one can attempt to derive I from (68) and (69).

6. Break-up of Jets. Formation of Emulsions

Many problems in connection with oil engines and the preparation of emulsions are concerned with the break-up of liquid jets. When a jet of liquid issues from a nozzle into the atmosphere, the jet eventually breaks up into drops under the action of disturbances to its figure of equilibrium. While some previous work, both theoretical and experimental, exists on the size and behaviour of the drops after formation, little quantitative work has been done on the fundamental aspects of the process of disruption. In particular, there is a lack of experimental data on the effect of ultrasonics on jets.

In the main there are two types of disruption. In the first, the interplay of inertia and surface tension results in swellings ("varicosities") of the cross-section of the jet. RAYLEIGH [30] considered the conditions under which symmetrical oscillations of this type, set up near the nozzle, might grow in amplitude. In a jet of small viscosity, he showed that a disturbance having a wave-length 4.4 times the diameter of the jet should increase most rapidly and eventually break up the jet into drops. In the other kind

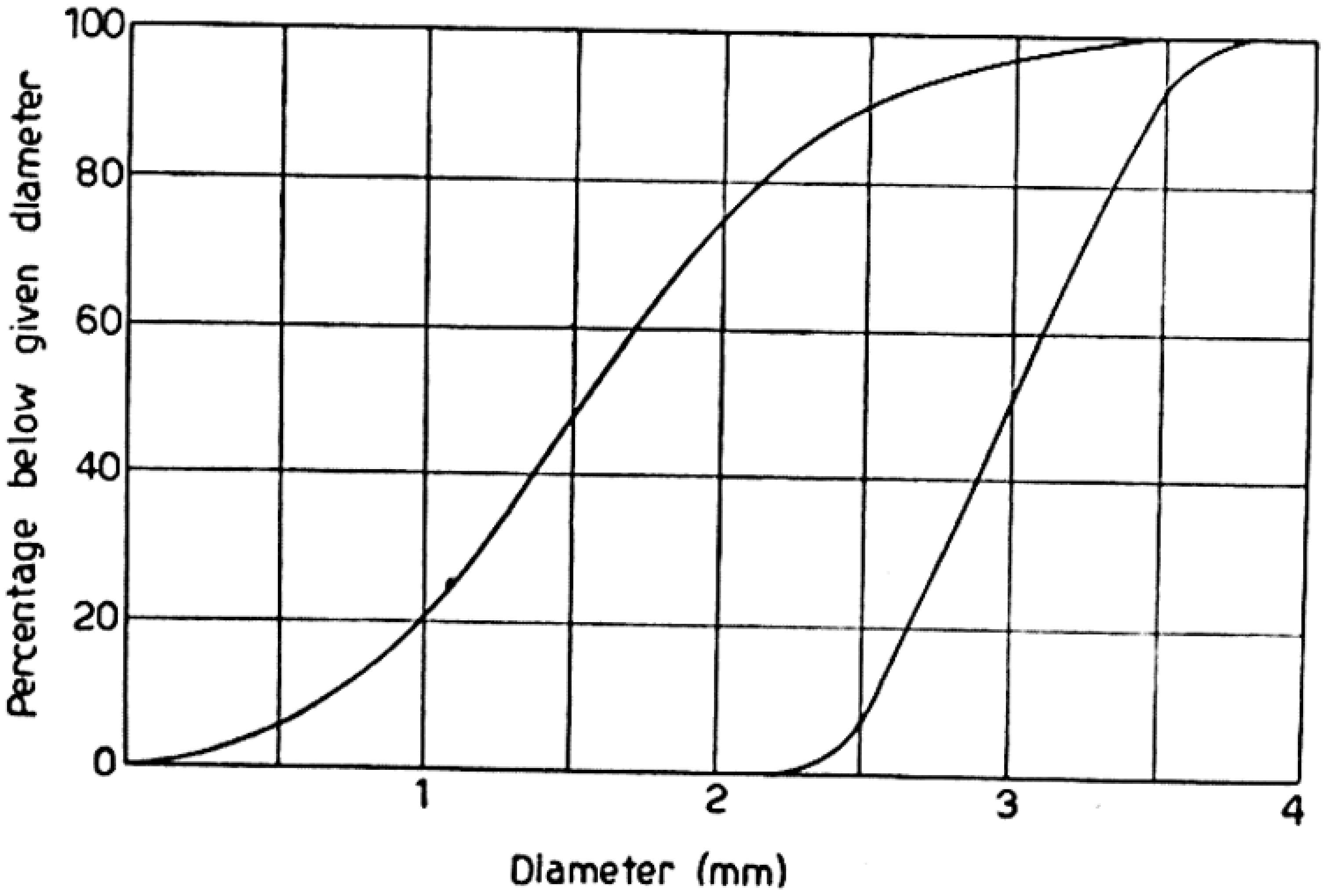

Fig. 99. Size Distribution of Droplets in Emulsion, with and without Ultrasonic Irradiation

of disturbance, the jet becomes sinuous and the resistance of the air to the crests of the waves becomes more important than surface tension. Viscosity affects the falling away from equilibrium in this type of flow as well as the rate at which waves on the jet grow. This kind is only amenable to experimental and empirical treatment. Fig. 99 shows two typical summation curves of the size: frequency distribution of a jet of oil entering water, varicose régime to the right, sinuous régime to the left.

One advantage in using ultrasonics to disrupt is that a fine dispersion into small drops of regular size is thereby produced.

It is preferable to apply ultrasonics to the one liquid only in this manner, instead of letting the two liquids stand one over the other in a tank, while the oscillator acts upon one or both of them. The latter method will, it is true, produce emulsions by breaking up the interface of the liquids, but, in general experience, does not produce a fine and regular dispersion such as one can get by acting on one of the liquids as it leaves the nozzle.

Work at the Centre National de Recherches at Marseilles, with the liquids in a tank and the oscillator under one of them, has shown that frequency and the relative viscosity exert peculiar effects. Some thin oils can emulsify in water at low and not at high frequencies, whereas viscous oils do the reverse. All this suggests that the two-phase method of forming emulsions is too complex for study in the laboratory.

References pp. 277–278

It has already been proved that ultrasonic agitation acting on the nozzle or on water in a tank into which oil is injected can cause a much finer break-up. Thus, if under conditions giving a dispersion curve like that on the right of Fig. 99, ultrasonic radiation acts on the jet, it at once changes to a type of break-up corresponding to that on the left, without any change in the speed of efflux (Richardson[31]).

If, however, the radiation acts on a fine emulsion already formed, it tends to coagulate the drops into larger ones, whereas an initially coarse emulsion becomes more finely dispersed under ultrasonic agitation.

It is evident that the break-up and coalescence of the particles in disperse systems is a complex phenomemon which requires further study for its elucidation.

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INDEX

OF SUBJECTS AND AUTHORS QUOTED

Abbey, R. L., 131

Abello, T. P., 107

Absorption in gases, 85, 105 *et seq.*, 152, 234

Absorption in liquids, 158 *et seq.*, 176, 206

Absorption in solids, 213 *et seq.*, 247

Acoustic birefringence, 260

Aerosols, 252, 269

Ahier, J., 18, 87, 168

Airgap, 11, 12

Alexander, A. E., 114, 118

Altberg, W., 256

Ammonium dihydrogen phosphate, 26

Andrade, E. N. da C., 33, 58, 260, 269

Anderson, N. S., 257

Anisotropic molecules, 243

Anomalous dispersion, 63, 65

Anomalous viscosity, 232

Ansford, D. N. E., 174

Attenuation; see Absorption

Ballon, J. W., 228

Bär, R., 217, 219, 220, 227

Barium titanate source, 26

Barlow, G. E., 131

Bastein, P., 270

Bauer, E., 224

Bazulin, P., 99

Becker, R., 127

Behn, V., 103

Belikov, P. N., 64, 244

Bell, J. F. W., 21, 79, 146

Bender, D., 136

Bergmann, L., 219

Bez-Bardili, W., 229

Bhagavantam, S., 99, 172, 222

Biquard, P., 181, 18, 55, 56, 87, 99, 160, 168, 173

Bömmel, H., 93, 261

Bleton, J., 270

Born, H., 53, 168

Boyle, R. W., 38, 214

Bradfield, G., 4, 28, 215

Brandt, O., 253, 269

Bubbles, 263

Brillouin, L., 173, 245

BUESCHE, A. M., 273
BUGOSH, J., 189
BURTON, C. J., 179
BUSS, W., 160

CADY, W. G., 23
Capillary tubes, 1, 148
CARSTENSEN, E. L., 266
Cavitation, 59, 266
CEROVSKA, J., 9
Characteristic impedance, 35, 54
Circuits for piezoelectric sorce, 14
— for magneto-strictive source, 24
Coagulation, 260, 267, 268
Condensed gases, 186
Critical angle of refraction, 221
— state, 140, 142
Crystallisation of melts, 270
Crystals, velocity in, 221
CURIE, P. and P. J., 3
Curie point, 13, 26, 28, 223
Curved source, 9, 229
Cuts of quartz, 4, 14, 22

DAVIES, N., 266
DEBYE, P., 96, 187, 191, 232, 273
DE BOCK, A., 55
DE KERVERSEAU, E., 272
Delay line, 170
Diffraction from source, 47, 33, 112, 168
— of light, 93, 173, 219
Diffusion coefficient, 262
Dispersion of matter, 267
Dispersion of velocity, 113, 128, 134, 136, 172, 234, 237, 244.
Dissociating gas, 127, 232
Double quartz interferometer, 77
Drops, 268, 275
DUDDELL, W., 2
DVORAK, V., 43
DWYER, R. J., 240
DYE, W. D., 8

ECKART, C., 58
Efficiency of source, 28
EINSTEIN, A., 232
Elastic liquids, 192
Electro-striction, 4, 28
Emulsions, 254, 275
EPSTEIN, P. S., 257
Equivalent circuit to quartz, 19, 75
ERNST, P., 229
EUCKEN, A., 127, 136
Examination of source, 8

FAIRBANK, H. A., 205
FAY, R. D., 56
Ferro-electric sources, 26
Fibres, 227
Fixed-path interferometer, 71, 112, 136, 139
Flexural vibrations of solid, 114, 219, 222
FOCKE, A. B., 223, 259
Focussing source, 9, 48
FOLDY, L. L., 226
FOX, F. E., 51, 76, 163, 185
Fraunhofer diffraction zone, 50, 168

Fresnel diffraction zone, 49
FREUND, H., 253, 269
FRY, J. and W. F., 242
—, W. J., 77

GALARIN, N., 259
GALT, J. H., 168, 184
Galton whistle, 1
Gas discharge and ultrasonics, 240
GEIGER, H., 103
GIACOMINI, A., 185
GIEBE, E., 218
GOGATE, D. V., 250
Grain refining, 270
Grating for ultrasonics, 64
— formed by wave train, 93, 173
GRIFFITHS, E., 137
GROBE, H., 99, 160
GROSETTI, E., 259
GROSSMAN, E., 107, 114, 233
GRÜTZMACHER, J., 9, 229
GUREVICH, S. B., 201
GUTH, E., 224

HALL, L., 245
HARDY, H. C., 76, 108
HARTIG, H. S., 81
Hartley circuit, 14, 17
HARTMAN, G. K., 259
Hartmann generator, 2
HAVORKA, F., 189
Helium II, 202, 248
HERGET, C. M., 139
HERMANS, J. J., 189
HERZFELD, K. F., 78, 232, 236
HIEDEMANN, E., 90, 219, 269
HILLIER, K. W., 228
HIMSTEDT, F., 104
HODGE, A. H., 137
HOESCH, K. H., 219
HOLTON, C., 181
HOLTZMAN, M., 256
HOPWOOD, F. L., 229
Hot-wire detector, 41, 52, 71, 105, 102, 123
HUBBARD, J. C., 44, 57, 74, 108, 114, 137, 143
HUDDART, D. R. A., 185
HUGHES, D. S., 221
Humidity, 120
HUNTER, A. N., 191
—, J. L., 185
HUZZARD, G. W., 177
Hydrosols, 268
Hypersonic velocity in liquid, 174, 245

Impedance of fluid column, 75, 196, 165, 243
— of source, 19
— of rubber, 226
Infra-red radiation and ultrasonics, 241
Interferometer for ultrasonics, 68, 107, 240
Ionic solvation, 187
IVEY, D. G., 224

JATKAR, J. K. K., 80, 116, 118
JEANS, J., 232

JEFFREY, G. B., 261
Jets, 274
JOHNSON, E. A., 40

KAWAMUR, H., 261
KELLER, H. H., 114
KENDALL, H. C., 135
Kirchhoff constant, 106, 132, 147, 176, 183, 239
KNESER, H. O., 107, 114, 125, 237, 244
KNUDSEN, V. O., 120, 125, 126
KOCH, P. P., 128
KÖNIG, K. W., 33, 269
KORNFELD, M., 266
KRASNOOSHKIN, P. E., 70, 85, 145
KRISHNAN, K. C., 172
KRUDRYATSEV, B., 242
Kundt's tube, 102
KURTZ, J., 12

LABAW, L. W., 9, 185
LAIDLER, T. J., 255
LAMB, H., 254
—, J., 176, 185
LAMBERT, J. D., 114, 118
LANDAU, L., 247, 248
LANE, H. A., 205
LANGEVIN, P., 4, 87.
LAWLEY, L. E., 151
LEHMANN, J. F., 38, 214
LENIHAN, J. M. A., 88
Lens, ultrasonic, 9, 229
LEONARD, R. W., 114
LEVAVASSEUR, G., 268
LIEBERMANN, L. N., 57, 246
LIEPMAN, H. W. ,186
LINDSAY, R. W., 45, 65, 221, 223
Liquid helium, 201, 248
Low temperatures, 143, 186, 204
LUCAS, R., 96, 173, 242, 248, 260
LUDLOFF, H. F., 218

MCCARTHY, J., 191
MCGRATH, J. W., 12
MCSKIMIN, H. J., 196, 227, 270
Magnetic field and ultrasonics, 242
Magneto-striction, 23, 28, 149
MARIENS, P., 144, 239
MALOV, N. N., 40
MASON, W. P., 10, 196, 199, 216, 227, 270
MATHIEU-SICARD, A., 268
MATOSSI, F., 172
MATTA, K., 116, 118
MAXWELL, J. C., 201, 237
MAY, J., 149
MEYER, E., 171, 263
Microphone detector, 45
MIKHAILOV, J. G., 201
MIMS, R. L., 221
Mists, 253, 257
Mixture of gases, 125
— of liquids, 178, 185
MOKHTAR, M., 118, 121, 242
Molecular absorption, 113
— effects in liquids, 174, 177, 244
MORSE, R. W., 215
Mounts for source, 11
MOURY, S. C., 224

MROWAN, A. B., 224
MULDERS, C. E., 170

Narrow tubes, 86
NATH, N. S. N., 97
NEKLEPAJEV, J., 106
NEUSCHELER, K., 40
NIKITINE, S., 261
NOLLE, A. W., 224
NORTON, G. A., 149
NUMANN, E., 136

OBERST, H., 105, 114
OBERT, L., 126
OKA, S., 189, 260
Optical examination, 43, 92, 218
— grating from ultrasonics, 90, 159
OVERBECK, O. J., 135
OZDOGAN, I., 114

PARBROOK, H. D., 140
PARIS, E. T., 40
PARKER, R. C., 260
PATHAK, P. D., 250
PARTHASARATHY, S., 97, 175
PEARSON, E. B., 260
PELLAM, J. R., 168, 184, 202, 208
PENMAN, H. L., 132
PESHKOV, J., 204
PETERLIN, A., 261
PETERSON, O., 93, 114
PHILLIPS, P., 142
PIELEMEIER, W. H., 121, 127
Pierce circuit, 14, 17, 24
PIERCE, G. W., 14, 24, 68
Piezo-electric source, 3
PINKERTON, J. M. M., 89, 168, 176, 185
Plates, transmission through, 36, 213, 216
Poisson's ratio, 219
Polymers, 227
PONDROM, W. L., 221
Pressure effect on gas, 128, 139, 143
— effect on liquid, 181
— of radiation, 38
PRICE, W. J., 223
Pulse generator, 18
— methods, 87, 168, 191, 223, 227
PUMPER, E. J., 130
Push-pull circuit, 14, 17

'Q' of source, 19, 55, 105
Quartz oscillator, 4
Quartz wind, 59
QUINN, J., 184

Radial modes in rod, 215
— modes in tube, 79, 85
Radiation from disc, 47
Radiometer, 37, 51, 168, 163
RAILSTON, W., 116, 118, 128
RAMAN, SIR C. V., 97
RANK, D. H., 174
RAO, B. V. R., 173
—, C. V. J., 99, 172
—, M. R., 174
RAPUANO, R. A., 169
RAWLINSON, J. S., 118

Rawlinson, W. F., 214

Rayleigh, Lord, 36, 56, 63, 80, 252, 279, 274

Reaction on source, 54, 70, 75, 164

Reflection at interface, 34, 73

— by disc, 36

Reid, J. A., 116, 127, 128, 130, 133 136

Reissner, N., 216

Relaxation, 201, 227, 247

Resistance thermometer, 40

Reverberation method, 170

Rice, J. C., 232, 236

Richards, W. T., 114, 116, 126, 127, 128, 130, 133, 136

Richardson, E. G., 40, 51, 108, 116, 121, 128, 140, 165, 192, 240, 254, 277

Rieckman, P., 164, 184

Ring source, 9

Rochelle salt, 26, 114, 223

Rock, G. D., 51, 163, 185

Rods, transmission through, 214, 218

Röhrich, K., 216, 218

Rogers, H. H., 121

Rosins, 201

Roth, W., 272

Rubber-like materials, 201, 217, 224

Ruedy, R., 214

Rufer, W., 179

Rumer, G., 247

Rutgers, A., 191

Sabine, P. E., 120

Sacerdote, G., 45

Satellite peaks, 79

Saxton, H., 127

Scattering, 61, 65, 243, 267, 270

Schaafs, W., 175

Schaefer, C., 219

Schallamach, A., 201, 232

Scheiber, A., 218

Schlichting, H., 58

Schlieren methods, 44

Schmidtmüller, N., 116

Scheoneck, H., 221

Schreuer, E., 172

Sears, F. W., 96

'Second Sound', 203

Seidl, Franciska, 190

Sette, D., 171, 229

Sewell, J. C. T., 252, 257

Shear waves, 192, 199, 219

Shear, S. K., 221

Shehata, M., 242

Sherratt, G. C., 137

Shull, E. R., 174

Silverman, S., 228

Singing arc, 2.

Smoke, 33, 253, 255

Smyth, J. B., 222

Sörenson, C., 38

Spakowski, B., 128

Specific impedance, 35

Sproule, D. O., 38, 214

Square wave generator, 18

Squire, C. F., 202

Steil, O., 114, 131

Stewart, J. L., 114
Stokes, G., 236, 254
Straubel cut, 9, 14
Streaming from source, 57
Strother, C. O., 114
Supersonic jet, 2
Suvorov, L., 266
Swanson, A. W., 81

Tamarkin, P., 66
Tamm, K., 263
Tawil, E. P., 8
Teeter, C. R., 127, 176
Telfair, D., 127
Temperature effects in gases, 132, 143
— effects in liquids, 183
— effect on source, 13
Thermal waves, 78, 203
Thurston, E. G., 266
Thys, L., 242
Tisza, L., 232
Toepler, A. M., 43
Torsional vibrations of solid, 9, 198, 218
Torsion vane, 36, 213
Transverse waves in solids, 220
Tube correction, 104, 145, 148
Tucker, W. S., 40, 105
Turner, A. N., 270

Van Dyke, K. S., 20
Van Paemal, O., 239
Van Itterbeek, A., 55, 143, 164, 186, 242
Vapours, 110
Variable path interferometer, 73, 143
Velocity in gases, 102 *et seq.*, 152, 233
— in fluids, 158 *et seq.*, 206
— in solids, 213 *et seq.*
Venkataswaran, C. S., 174
Vermeulen, R., 144
Vincent, J. H., 24
Visco-elastic fluid, 192
Viscosity in fluid, 86
Vladimirski, V., 259

Walti, A., 217, 219
Warner, G. W., 135
Wave-form in fluid, 56
Webber, R., 104
Wilks, C. R., 223
Willard, G. W., 179, 227
Williams, A. O., 185
Witte, R. S., 224
Wright, J. V., 257

Yeager, E., 189

Zachoval, I., 172
Zartman, C., 131
Zvetkov, V., 263

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